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Investigating pedogenic carbonate formation by measuring the stable isotope composition of water in Vertisols

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Investigating pedogenic carbonate formation by measuring the stable isotope composition of water in Vertisols

by

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Dedication

I would like to dedicate this thesis to a group of special people. But first, I would like to give honor and praise to the Lord Almighty for his grace, guidance, blessings, and love through my entire life. This dedication is for my family, friends, mentors, girlfriend, and colleagues that has given me encouragement, happiness, knowledge, advice, and love that has led me to the completion of this thesis. Thank you'll for being in my life and may the Lord bless you as you have me with your presences.

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Abstract

Investigating pedogenic carbonate formation by measuring the stable isotope composition of water in Vertisols

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The oxygen isotope compositions of pedogenic carbonates in paleosols are used to reconstruct paleoelevations, paleoatmospheric circulation, paleotemperatures, and paleoprecipitation. The oxygen isotope compositions of pedogenic carbonates are controlled by temperature and the oxygen isotope composition of soil water, which predominately originates from precipitation. In most calcic soils studied, pedogenic carbonates record the oxygen isotope composition of summer precipitation and/or mean annual precipitation subjected to evaporation. However, due to the complex hydrological properties of Vertiols, which are abundant in the rock record, the isotopic composition of soil water could potentially vary and could influence the isotopic composition of pedogenic carbonate. Furthermore, it is well established that soils contain multiple pools of water with different stable isotope compositions but little work has been done to investigate which pools are recorded by pedogenic carbonates. Therefore, the isotopic composition of soil water in modern Vertisols was monitored and compared with the oxygen isotope composition of pedogenic carbonate in the same soils to investigate if the oxygen isotope composition of pedogenic carbonates in Vertiols record mobile or immobile water.

The isotope composition of soil water was determined in four ways: 1) measurement of isotope composition of water collected by vacuum distillation of soil samples collected by auger, 2) calculation from measured oxygen isotope compositions of soil CO_2, 3) calculation from measured oxygen isotope compositions of pedogenic carbonate, and 4) measured isotope compositions of water collected under tension in a soil solution sampler. The oxygen isotope

compositions of water in equilibrium with CO_2 and water from the solution sampler were indistinguishable at 140cm and were interpreted as mobile water in macropores. The vacuum distilled water (which includes water from a mixture of macropores and micropores) always had lower $\delta^{18}O$ values than the macropore water and the other sampling methods, implying the presence of water with low $\delta^{18}O$ values. These oxygen isotope compositions of soil water pools were compared with $\delta^{18}O$ values of local precipitation (GNIP data from nearby Waco, TX). Below ~100cm, total soil water $\delta^{18}O$ values converge to -6.3 ± 0.7 ‰ (1σ, n=20), which is isotopically lighter than the $\delta^{18}O$ of mean annual precipitation (MAP) of Waco, Texas (-3.8 ± 2.7 ‰, 1σ, n=96). This could result from recharge of isotopically light September precipitation (SEPT); (-5.9 ± 2.4 ‰, 1σ, n=8)) replenishing the soil after dry periods and/or the contribution of winter precipitation (WP) (-5.5 ± 2.4 ‰, 1σ, n=25). The $\delta^{18}O$ values of soil water in equilibrium with soil CO_2 ((-4.1 ± 0.8‰) are isotopically similar to or heavier than the isotopic composition of MAP. The $\delta^{18}O$ values of soil water in equilibrium with pedogenic carbonate (-2.7 ± 0.9‰) are also isotopically similar to the isotopic composition of summer precipitation (SP, including June, July, and August) (-2.0 ± 2.9 ‰, 1σ, n=8). This suggests that, despite the more complex hydrology of Vertisols compared with other soils orders, the $\delta^{18}O$ values of pedogenic carbonates formed in central Texas Vertisols record SP and/or mean annual precipitation that has been subjected to evaporation, just as they do in other soils. If this holds true for Vertisols formed in other climates, then this facilitates the comparison among $\delta^{18}O$ values of paleosol carbonates from various soil orders, which is common practice in vertical successions of paleosols. Furthermore, the observation that the $\delta^{18}O$ values of water in equilibrium with pedogenic carbonate are more similar to the $\delta^{18}O$ values of macropore than micropore water suggests that pedogenic carbonates in central Texas Vertisols may form in macropores. Formation in macropores is more consistent with CO_2 degassing and/or evaporation, rather than root water uptake, as a proximal driver of calcite precipitation.

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Chapter 1: Introduction

Pedogenic carbonates occur globally in soils of semiarid climates and are among the best studied features of buried soils and paleosols. In particular, oxygen isotope compositions of these carbonates are used to reconstruct paleoelevations (e.g., Garzione et al., 2000), paleoatmospheric circulation (e.g., Amundson et al., 1996), paleotemperatures (e.g., Dworkin et al., 2005), and paleoprecipitation (e.g., Retallack, 2005). The oxygen isotope compositions of pedogenic carbonates are controlled by temperature and the oxygen isotope composition of soil water, which predominately originates from precipitation (e.g., Cerling, 1984; Cerling and Quade, 1993). Paleoenvironmental studies typically assume that the oxygen isotope composition of pedogenic carbonate records the isotopic composition of mean annual precipitation (MAP). However, it is well established that soils contain multiple pools of water with different stable isotope compositions (e.g., Brooks et al., 2010; Landon et al., 1999) and little work has been done to investigate which pools are recorded by pedogenic carbonates. In this study, we compared the oxygen isotope compositions of mobile and immobile soil water pools with coexisting pedogenic carbonate in modern Vertisols to determine which of these pools is recorded by the carbonate.

Chapter 2: Background

2.1 Soil water

Soil water is an important resource that influences the transport of dissolved species, translocation of salts, and can be a reliable water source for plants during periods of droughts. Precipitation is the main source of soil water in areas where irrigation is not present and the water table is too deep to replenish surface soil moisture lost from evapotranspiration (ET). After water from precipitation has fallen onto the ground surface, it will either runoff, return to the atmosphere through ET, or percolate into deeper soil below the influence of ET. The percolated water is then influenced by three processes based on the soil properties (texture, organic matter content, water content): piston flow (new water pushes older soil water deeper through the soil), pure mixing (new water mixes with older soil water), and preferential flow (new water bypasses older soil water through large pathways, such as cracks) (Kladivco et al., 1999; Cook et al., 2010; Beven and Germann, 1982). Water in the vadose zone can generally be classified as either mobile or immobile (Genuchten and Wierenga, 1976). Mobile water is driven by gravitational flow and located in macropores, which are characterized by either the pore size distribution or water flow and are defined by having an equivalent cylindrical diameters larger than 0.3 to 0.5 mm through which water can flow (Jarvis et al., 2007). Immobile water occurs in the stagnant zone inside soil aggregates (micropores), where matric potential and diffusive transport dominate. The relative proportion of immobile water to total soil water content is high during unsaturated conditions (typically maximum in the summer) whereas the relative proportion of mobile water is high during saturated conditions (typically maximum in the winter).

Past studies have observed that the mobile and immobile water do not readily mix with one another (de Smedt and Wierenga, 1979; Gerke and van Genuchten, 1993; Gao et al., 2010; Brooks et al., 2010). These studies suggest that mass exchange between the mobile and immobile zone is dominated by diffusion processes (Genuchten and Wierenga, 1976; Jaynes et al., 1995), which occurs slower than the advection – dispersion (gravitational) processes that dominate water flow in the macropores. This slow mass-exchange can lead to the isotopic composition of soil water in micropores and macropores that are different (Brooks et al., 2010).

The isotopic composition of soil water has been used to understand various processes occurring in the soil such as ET (Gat and Tzur, 1967; Zimmermen et al., 1967a; Allison, 1982;

Allison et al., 1983; Walker et al., 1988; Barnes and Allison, 1989, Depaolo et al., 2004), mixing and percolation (Gazis, 2004; Hu et al., 2008), infiltration processes (Liu et al., 1995; Mathieu and Bariac, 1996), recharge rates to aquifers (Fontes et al., 1986; Simpson et al., 1990), water uptake by plants (Ellsworth, 2006), and adsorption to clay surfaces (Stewart, 1972; Coplen and Hanshaw, 1973; Phillips and Bentley, 1987). Previous studies have reported differences in the isotopic composition of mobile and immobile waters (Landon et al., 1999; Zhao et al., 2013). These investigators used different soil water collection methods (suction lysimeter, cryogenic vacuum distillation, etc.) to separately collect mobile and immobile waters. They concluded that suction lysimeters collect water in macropores (mobile water) with isotopic compositions similar to recent rain events; whereas, the vacuum distilled water is the total water (mobile and immobile waters) with isotopic compositions that vary with the relative abundance of mobile and immobile waters. Brooks et al. (2010) suggest that the $\delta^{18}O$ values of precipitation vary throughout the duration of larger events that rewet the soil after dry seasons. Here, the initial precipitation that rewets the soil near the surface is isotopically heavier. Subsequent precipitation within the storm is isotopically lighter and bypasses the shallow soil and rewets the deep soil. Therefore, an isotopic gradient is produced toward lighter values with depth.

These studies illustrate that the isotopic composition of soil water is divided between mobile and immobile regions of the soil. Highly structured clayey soils, such as Vertisols, can have complex structures that could lead to different proportions of mobile and immobile water, which could influence the isotopic composition of pedogenic carbonate in these soils. In this study, we investigated isotopic compositions of mobile and immobile water to determine which is recorded by soil carbonate in Vertisols.

2.2 Properties of Vertisols

Many paleosols used to understand past climate and environments are Vertisols, which are clay-rich (greater than 40%) soils that swell when wet and shrink when dry (Wilding and Tessier, 1988). Vertisols occur extensively in seasonally dry regions of the tropics and subtropics (Virmani et al., 1982). Globally used for agriculture due to their high water-holding capacity, Vertisols have the ability to store sufficient water that supports vegetation through periods of drought. Repeated shrinking and swelling results in the development of microtopographic

features (gilgai and subsurface waviness), which can be observed as microhighs and microlows (depressions) on the soil surface. The development of microtopography leads to drastic changes in the properties of the soil (Nort and Driese, 2009).

During periods of warm temperature and low precipitation, large cracks will form in Vertisols, due to decreasing soil moisture and shrinkage of the soil. Studies have suggested that these large cracks (meters in depth) allow water to bypass the surface resulting in preferential flow to deeper portions of the soil (Beven and Germann, 1982). Other studies have discovered the existence of immobile water, which is strongly held in interaggregate micropores, dead-end pores, or adsorbed to grain surfaces (Gvirtzmann and Magaritz, 1986; Edmunds et al., 1991; Coulomb et al., 1993).

The complex properties within Vertisols make stable isotopic analyses of soil water complicated to link to specific processes within the soil (Wilding and Coulombe, 1996; Driese et al., 2000). Mathieu and Bariac, (1996) showed that preferential flow of water through cracks in soil profiles results in the isotopic composition of deep soil water to be similar to local precipitation. They also observed that the immobile water enriched by evaporation near the surface will mix with incoming water affecting the isotopic composition of soil water. In laboratory experiments, isotopic fractionation was observed when water was forced through a compacted disc of clay (Coplen and Hanshaw, 1973). The $\delta^{18}O$ values of this ultrafiltrated water (mobile water) was depleted in δD by 2.5 ‰ and $\delta^{18}O$ by 0.8‰, relative to the isotopic composition of the initial water. A potential explanation for this observation is that the organized structure of water in hydration spheres around cations adsorbed to clay surfaces preferentially concentrates DHO and $H_2{}^{18}O^{16}O$ over H_2O (Philips and Bentley, 1987). If this process occurs as water percolates through soils, the retained water (mainly immobile water) would have a higher δD and $\delta^{18}O$ values, which would lead to a progressively lower delta values with depth. These processes are important to consider for the study of oxygen isotope compositions of pedogenic carbonates in Vertisols, because the $\delta^{18}O$ values of soil water control the $\delta^{18}O$ values of pedogenic carbonates.

2.3 Pedogenic carbonate

Pedogenic carbonates (typically calcite) occur as nodules, filaments, clast coatings, and cemented carbonate horizons that precipitate from aqueous solution in soils. In Vertisols, pedogenic carbonates typically accumulate as nodules and/or filaments. The oxygen isotope composition of pedogenic calcite is controlled by the isotopic composition of soil water and the temperature-sensitive equilibrium isotope fractionation factor between calcite and water (Cerling, 1984; Cerling and Quade, 1993, Kim and O'Neil, 1997).

Comparisons between the oxygen isotope composition of pedogenic carbonate in Holocene soils with the oxygen isotope composition of local precipitation, suggests that pedogenic carbonate records the isotopic composition of local summer precipitation and/or soil water that is isotopically heavier than isotopic composition of MAP, possibly due to evaporation (e.g. Cerling and Quade, 1993; Liu et al., 1995; Peters et al., 2012; Quade et al., 2013; Hough et al., 2014). However, this may or may not be applicable for Vertisols given their complex hydrology. For instance, presences of large cracks could lead to a preferential recharge during larger summer precipitation events, which would likely have an isotopic composition different than mean summer precipitation. Additionally, the isotopic composition of pedogenic carbonate could potentiallly be influenced by water in either macropores (mobile water) or micropores (immobile). Previous studies have suggested that carbonate precipitation is catalyzed by and can form on the surface of clay minerals (e.g. Quigley et al., 1985; Tonnisen et al., 1985; Kralj and Vdovic 1999) and could therefore record micropore water.

Although, the stable isotope compositions of pedogenic carbonates have been widely used as a tool to address paleoenvironments, little is known about the time and location (macropores verses micropores) for pedogenic carbonate formation in Vertisols. Therefore, the purpose of this study is to compare oxygen isotope compositions of soil water and pedogenic carbonate in modern Vertisols to determine what the oxygen isotope composition of pedogenic carbonate in Vertisols records. The specific scientific questions we seek to answer are (1) what type of water (mobile or immobile) does the isotopic composition of pedogenic carbonate records and (2) does deep soil recharge occur in the summer (due to cracking) or winter season (low ET).

Chapter 3: Methods

3.1 Field work

3.1.1 Field Sites Descriptions

Three field sites were investigated for this study; soil at each site desiccates during the summer due to high ET, leading to the development of large cracks (meters in depth). The first field site, Richland Creek Wildlife Management Area (RCWMA), is a Trinity River floodplain Vertisol located near Fairfield, Texas (35°53′50″N 93°27′26″W). The soil is a fine, smectitic, thermic, Aquic Hapludert (Trinity and Kaufman clays). RCWMA is located between the Post Oak Savannah and Blackland Prairie ecological regions. The site is vegetated as a bottomland hardwood forest dominated by cedar elm [Ulmus crassifolia] and hackberry [Celtis occidentalis] with a minor amount of green ash [Fraxinus pennsylvanica]. Standing water, a meter in depth, has been reported at the site and some degree of ponding was observed during the study. The second field site, USDA-ARS Riesel Watersheds, near Riesel Texas (site RI, 31°28′20″N 96°55′55″W), is a mixed C_3-C_4 grassland located on an upland hillslope. The soils at this site belong to the Houston Black and Heiden series, both of which are fine, smectitic, thermic, Udic Haplusterts. The vegetation consists of C_4 bunch grasses (primarily little bluestem [*Schizachyrium scoparium*], sideoats grama [*Bouteloua curtipendula*], big bluestem [*Andropogon gerardii*], and Indian grass [*Sorghastrum nutans*]) and various C_3 forbs (Breecker et al., 2013). Samples were collected along the same catena studied by Breecker et al. (2013) and Michel et al. (2013). The RCWMA and RI both have mean annual precipitation of 102 cm. The last field site, Dance Bayou (DB) (28°52’00’’N, 95°32’00’’W), is a floodplain for the Brazos River and has a mean annual precipitation of 114 cm (http://www.ncdc.noaa.gov/). This site also hosts a bottomland hardwood forest, similar to RCWMA. The soil at this site belongs to the Churnabog series, which are fine, semectitic, hyperthermic, Aeric Calciaquerts. The site typically ponds with 10 cm of rain water in microlows during the winter. The study location is the same as that studied by Mintz et al. (2011) and Miller and Bragg (2007). Samples (water, soil, calcium carbonate, and soil CO_2 samples) were collected semi-periodically (~ once every two months (1 per 2 months)) from RCWMA; however, sampling at RI and DB was limited to a single event. RCWMA and DB pedogenic carbonate samples were collected from a trench excavated by a backhoe, during which soil descriptions were done. RI carbonate samples were collected from

cores using a Giddings Probe. The three site can been seen in a google map of Texas in figure 1.

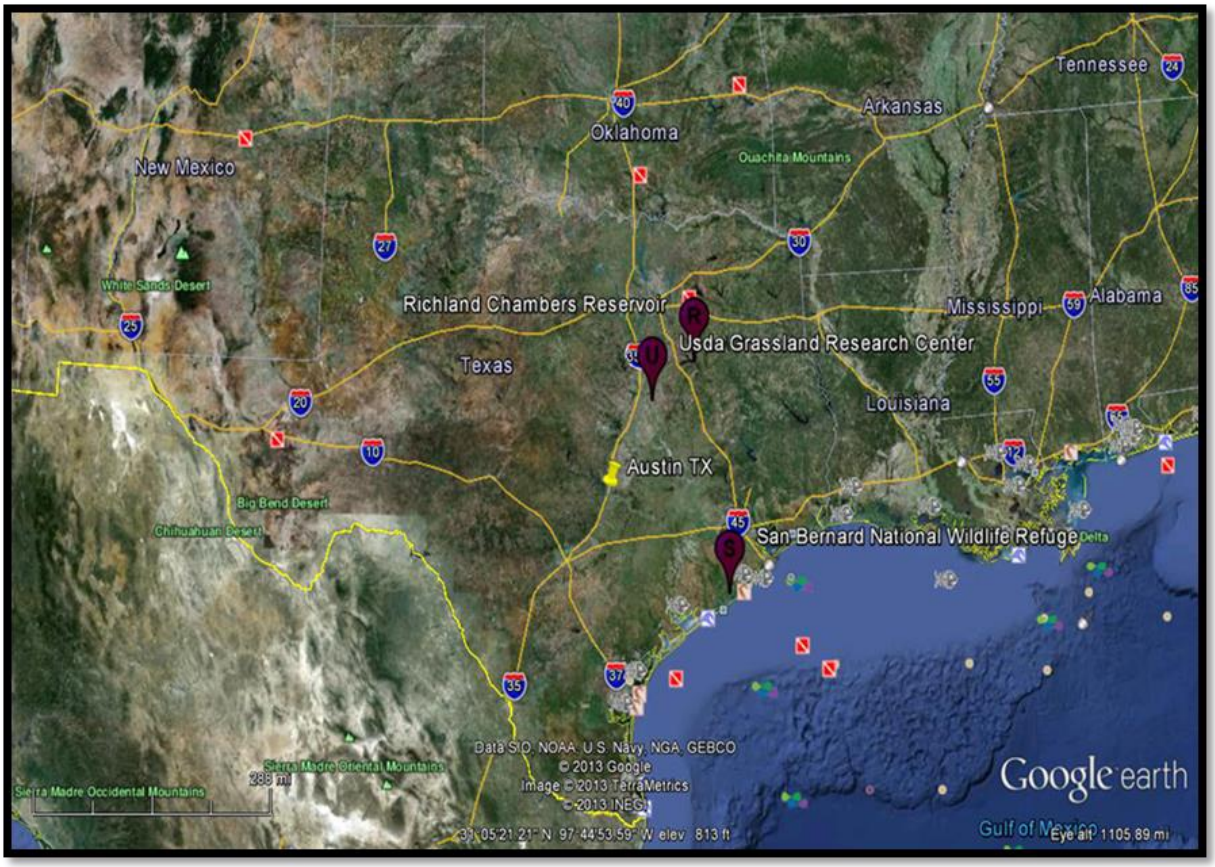

Figure 1: Google map of Texas indicating the location of the RCWMA (balloon with an R), RI (balloon with a U), and DB (balloon with an S) field sites

3.1.2 Soil Water

Soil water was collected from the soil in two ways, cryogenic vacuum distillation (total soil water) on bulk soil samples returned to the laboratory and soil solution sampler (mobile water) in the field. Soil samples were collected semi-periodically (approximately every 2 months) from the Richland Creek Wildlife Management Area to monitor seasonal changes. For every field visit, bulk soil samples from four soil profiles were collected, three from microlows and one from a microhigh. We focused on microlows because pedogenic carbonates in microlows are more likely to have formed in situ, whereas pedogenic carbonate in microhighs are more likely to have been translocated within soil by shrink-swell induced soil deformation. Bulk soil samples from one microlow and the microhigh were collected at seven different depths (10, 20, 40, 60, 80, 100, and 140 cm). For the other two microlows, samples were collected at three depths (10, 30, 140 cm). Samples were collected using a 7.5-cm diameter mud auger. Holes were augured approximately 50 to 100 cm away from large trees to avoid tree roots. Grass and leaf litter were removed from the surface to prevent this loose material from falling down the auger hole and contaminating subsequent samples. Immediately after removal from the auger bucket, each soil sample (~7 grams) was stored in a glass test tube, sealed with rubber stoppers (with parafilm until August 2013) to prevent evaporation. After sampling, auger holes were backfilled and marked to avoid resampling. Soil samples at RI and DB were collected using this same method, except that samples were collected only from microlows and only one time (August 21, 2013 at RI and August 16, 2013 at DB). Two profiles were sampled at RI, one located at the toe of the slope (near well 'A' of Breecker et al. [2013]) and the other at a mid-slope position (near wells 'C' of Breecker et al. [2013]). Sampling intervals at RI were similar to RCWMA, except that one sample from the down-slope was collected at 120 cm instead of 100cm. Samples from four profiles were collected from DB at depths of 10, 30, 70, 100, 150 cm.

A solution sampler (model SW 071, Soil Measurement Systems, Tucson, AZ) was installed in a microlow location at RCWMA in October 2013 to collect mobile soil water. The opening of the solution sampler was installed at a depth of 140 cm and backfilled with dried and crushed soil from this site. A tension of 300 millibars was applied to collect soil water into the sampler's reservoir. The collected water was then removed by applying positive air pressure.

Approximately 120 ml of water was collected from the solution sampler for isotope and chemical analyses.

3.1.3 Meteoric Water

A 500 ml plastic carboy, 1.25 cm funnel, and a plastic ball valve were used to construct the precipitation collector, which was installed in December 2012. During every field visit, a meteoric water sample was collected from the precipitation collector and the volume of water in collector was measured and recorded. The precipitation collector was drained and prepared for future rain events. Between June 2013 and December 2013, the precipitation collector was damaged and no samples were collected during this time. On January 2014, another precipitation collector was created out of a 5 gallon plastic bucket and installed. A layer of mineral oil at least 2.5 cm thick was maintained in both precipitation collectors to minimize evaporation. Meteoric water samples were analyzed for hydrogen and oxygen isotope ratios.

3.1.4 Soil CO_2

Beginning in May 2013, soil gas samples were collected from the three sites for measurement of $\delta^{18}O$ values of soil CO_2. All soil gas samples reported here are from microlows. Soil gas samples were collected from soil gas wells of the design described by Breecker et al. (2013). Briefly, the wells were constructed from perforated 3.2 cm PVC tubing and were waterproofed with Ultrex® 2-Ply (www.seattlefabrics.com), which was fixed to the PVC with silicone (RCWMA and DB wells only, RI wells were not waterproofed). The wells were installed into auger holes. An epoxy-coated tip thermocouple (model TC-PVC-K-24, Omega Engineering, Stamford, CT) was buried into wells LC 95, LD 17, LD 60, LD 113, and LE 135 for measurement of soil temperature (Breecker et al., 2013). Dried soil from the RCWMA site was crushed and used to backfill holes after well installation at that site. Bentonite clay was used to backfill holes at the RI site and wet soil was used to backfill at DB.

Soil gas was collected by syringe (3 mL volume) that was used to penetrate a rubber septum sealing the above-ground section of the well. Prior to sample collection, the syringe was purged once with soil gas. On the second penetration, the syringe was pumped three times to obtain a sample representative of the soil gas. The 3 mL samples were then extracted and injected into UHP He-flushed 12 ml vials (model 736W, Labco International Inc., Houston, TX). Duplicate samples were collected from each soil-gas well to evaluate precision. From RCWMA,

seven soil gas samples from different depth ranges were collected, including a three-well profile from a single microlow. The depths of the wells in the microlow three-well profile were 17-24, 68-80, and 121-135 cm. Last four samples were from depth ranges of 95-104 cm, 120-140 cm, 113-127 cm, and 142-155 cm. From RI, four gas samples were collected from different depth ranges within one profile. The profile depth ranges were 54-65 cm, 77-88 cm, 93-104 cm, and 112-123 cm (see Breecker et al. [2013] for gas well locations). From DB, six gas samples were collected from different depth ranges within one profile. Three sample ranges collected in the same profile were 64-76, 63-77 and 92-106cm. The last three depth ranges from other locations were 45-59, 91-105, and 119-133cm.

3.2 Laboratory Methods

3.2.1 Cyrogenic Vacuum Distillation (total water)

Cryogenic vacuum distillation, similar to the method in West et al. (2006), was used to extract water from soil samples for isotopic analysis. Glass test tubes (25mm diameter, hereafter referred to as sample tubes) used for storing soil samples were attached directly to the glass line and sealed with an O-ring including the threaded connection part and a nylon bushing (model 7644-20 and 7506-10, Ace Glass, Vineland, NJ, figure 2). A filter (model 548-14, Ace Glass, Vineland, NJ) was used to prevent soil particles from entering the glass line. Then, the test tube holding the soil samples was submerged into liquid nitrogen to freeze all water to prevent water loss during air removal. Opening valves 1 and 2 (figure 2) applies a vacuum to the sample tube and the glass tube, where distilled water was collected (collecting tube) to remove the non-condensable gases (air). Air removal before water distillation is important to optimize water extraction. Air removal was difficult because substantial amounts of air sorbed to these high surface area soil samples at liquid nitrogen temperatures. Therefore, four molecular sieve 5A (model B21109, Alfa Aesar, Heysham, UK) loaded into the collection tube were used to remove adsorbed air during the distillation of water that would otherwise interfere with the vacuum. Small (2 mL) of distilled water standards (Austin DI water, $\delta D = -3.4 \pm 0.3‰$) with and without zeolites were analyzed and a 0.2‰ difference in the δD values were observed (Table 3A). Removing the liquid nitrogen, samples were allowed to thaw to release any remain sorb air in the

soil. Air removal processes were repeated. The average time for air removal was 2 hours and 30 minutes.

After air removal, water extraction began by closing valve 1, resulting in a constant pressure in the section of the glass line below valve 1(including the glass arm, glass attachment, collecting tube, sample tube). The sample tube was placed into hot water (at 100°C) to evaporate the soil water. At the same time, the collecting tube was placed in liquid nitrogen to condense and thereby collect the water. The average time for water extraction was 1 hour and 30 minutes.

Complete distillation was tested by three methods. First, liquid nitrogen was raised above the collecting tube to observe condensation of water vapor on the side of the glass tube. If no water condensed, then the extraction was near completion. Secondly, valve 1 was slightly opened to measure the pressure in the distillation volume, which indicated whether or not a fraction of the total water was still water vapor and had not yet condensed in the collecting tube. If the pressure did not increase when valve 1 was opened, this demonstrated that all water was transferred to the collecting tube. Lastly, the mass of water collected was compared to the mass difference between the mass of the soil before and after extraction (calculated water mass). All samples plotted within 95% of the 1:1 line, demonstrating that all water was collected during water extraction resulting in no fractionation in the sample (figure 12A). After distillation was complete, water samples were transferred into 2 mL glass vials and gravimetric water content was calculated.

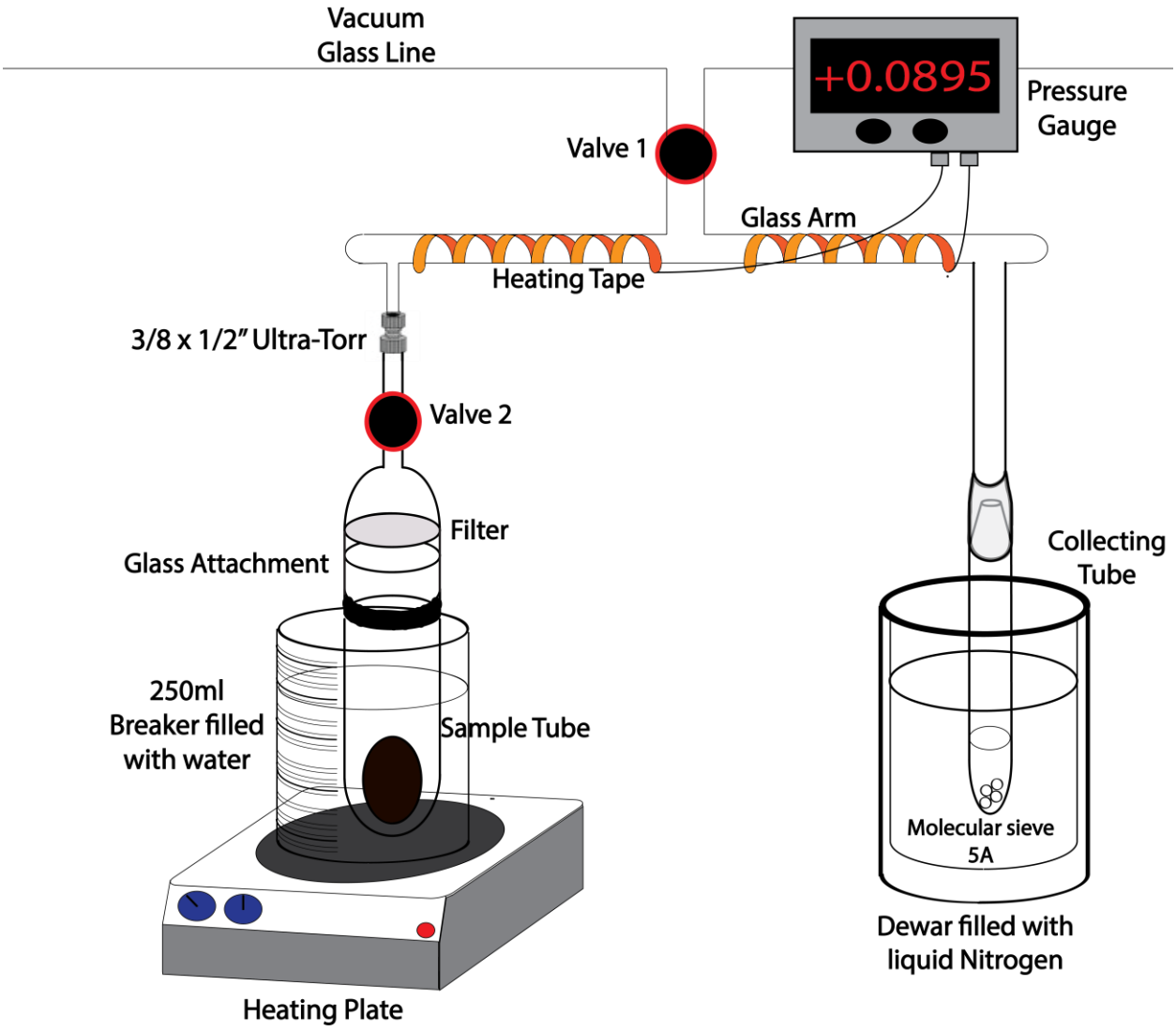

***Figure 2**: Schematic for cyrogenic vacuum distillation*

3.2.2 Gravimetric water content

Gravimetric water content was determined by weighing samples before and after distillation on the vacuum line. To prevent evaporation of soil water samples, the sample tube used to store soil samples, rubber stopper, and soil sample were all weighed together in the laboratory. After water extraction, sample tube with stopper/parafilm and dry soil sample were reweighed. The dry sample mass was subtracted from the initial sample mass to calculate the

mass of water extracted. Then, the dry sample was weighed alone and divided from the distilled water mass to obtain the gravimetric water content of each sample.

3.3 Isotope Ratio Mass Spectrometry

3.3.1 Water: Oxygen and Hydrogen isotopes

The stable isotope compositions of soil water samples were measured in the University of Texas at Austin Stable Isotope Laboratory for Critical Zone Gases. The oxygen isotope ratios were measured using an isotope ratio mass-spectrometry (IRMS) (Thermo Scientific MAT 253 and Gasbench II) and autosampler (PAL) operating in continuous-flow mode. A 1 mL of aliquot water was injected into 12 mL septum-capped vials (model 736W, Labco International Inc., Houston, TX) previously flushed with a mixture of CO_2 (3000 ppmV) and He (balance). The CO_2 was allowed to equilibrate with the water at 25°C for 24 hours before analysis by multiple loop injections through the Gasbench, a modification of the original CO_2 equilibration technique described by Epstein and Mayeda (1953). The water-equilibrated CO_2 was analyzed against a reference gas of known isotopic composition. Measured oxygen isotope compositions are reported relative to the Vienna Standard Mean Ocean Water standard (VSMOW) and were adjusted to that scale by comparison with internal laboratory standards calibrated such that the $\delta^{18}O$ value of the Standard Light Antarctic Precipitation (SLAP) is -55.5 relative to (VSMOW) (Coplen et al., 1983). The external reproducibility of repeated analyses of standards averaged ±0.07‰ for $\delta^{18}O$ (1σ). Hydrogen isotope compositions of water samples were measured in continuous-flow by reduction to H_2 with a thermal conversion elemental analyzer (TC/EA) (Thermo Electron) followed by analysis of H_2 using the IRMS. Measured hydrogen isotope compositions are reported relative to VSMOW and were adjusted to that scale using internal laboratory standards calibrated to VSMOW and SLAP. The external reproducibility of repeated analyses of standards averaged ±0.89‰ for δD (1σ).

3.3.2 Soil CO2

Soil CO_2 samples were measured for oxygen isotopic composition at the University of Texas at Austin Stable Isotope Laboratory for Critical Zone Gases using the continuous-flow IRMS method described by Breecker and Sharp (2008). Samples were analyzed within 24 hours of collection to minimize the effects of oxygen isotope exchange inside the vials (e.g. Breecker

and Sharp, 2008). Aliquots of appropriate size were transferred by valved syringe (valve closed during transfer) from collection vials into newly flushed vials for analysis. Samples were flushed from the analysis vials in a He stream and directed through a liquid nitrogen cooled trap using a Gasbench II. The cryofocused CO_2 was analyzed as a single pulse in continuous flow mode. This process had to be repeated for some samples to achieve the appropriate signal voltage (5-20V) in the mass spectrometer. Measured $\delta^{18}O$ values are reported relative to the Vienna Pee Dee Belemnite standard (VPDB) and were adjusted to that scale using internal laboratory standards calibrated by comparison with CO_2 gas equilibrated with water standards (Greenland Ice Sheet Precipitation standard (GISP), VSMOW, and SLAP) and with a National Oceanic and Atmospheric Administration (NOAA)-calibrated CO_2-in-air cylinder.

3.3. 3 Soil Carbonate

Samples of soil carbonate nodules that likely formed in-situ within the soil at RCWMA from depths between 120 and 150 cm were drilled from soil thick sections. Oxygen isotope ratios of the drilled powders were measured at the University of Texas at Austin Stable Isotope Laboratory for Critical Zone Gases using the continuous-flow IRMS method described by Spötl and Vennemann (2003). Measured oxygen isotope compositions are reported using standard δ-per mil notation relative to VPDB and were adjusted to that scale using internal laboratory standards calibrated against the National Bureau of Standards (NBS) 19 = -2.2 and NBS 18 = -23.2. The external reproducibility of repeated analyses of standards is better than 0.1‰ (1σ) for $\delta^{18}O$. Soil carbonate was collected and analyzed once assuming that the isotopic composition of pedogenic carbonate in these soils does not change during the interval of investigation. The $\delta^{18}O$ values of calcium carbonates in the RI and DB soils were taken from Michel et al. (2013) and Mintz et al. (2011), respectively.

Chapter 4: Results

4.1 The isotopic composition of total soil water (vacuum distilled water)

The hydrogen and oxygen isotope compositions of vacuum distilled soil water are listed in Table I. The differences between the isotopic compositions of soil water in microhigh and microlow locations at RCWMA ranged from 2.0‰ to 0.0‰ with an average of 0.6 ± 0.5‰. The isotopic composition of vacuum distilled water from microlows is most appropriate for comparison with the isotopic composition of water in equilibrium with CO_2 and water from the solution sampler, because the soil gas wells and the solution sampler were installed in microlows. The pedogenic carbonate was also collected in a microlow location, and therefore only considers the vacuum distilled water from microlows. Figure 3 shows the results of the total water collected at RCWMA.

***Table I**: The $\delta^{18}O$ values, δD values, and water content for vacuum distilled soil water from RCWMA collected from microlows. The numbers with (*) are replicates at that specific depth. The $\delta^{18}O$ and δD values are reported relative to VSMOW.*

Date	Depth (cm)	$\delta^{18}O$ (‰)	δD (‰)	θ (%)
21-Sep-12	10	-3.5	-27.4	29.0
	20	-2.9	-20.6	35.0
	30	----	---	---
	40	-4.3	-30.8	21.0
	60	-7.3	-31.1	19.0
	80	-6.5	---	---
	100	-3.8	-28.5	---
	140	----	---	---
17-Dec-12	10	-6.3	-41.2	41
	20	-7.8	-46.6	35
	30	---	---	---
	40	-6.2	-35.0	30
	60	-6.7	-36.7	29
	80	-6.8	-38.3	27
	100	-6.7,-6.2*,-6.5*	-41.9, -36.3*	16, 22*, 18*
	130	-7.0, -7.0*	---	24
28-Feb-13	10	---	---	---
	20	---	---	---
	30	-5.1, -6.5*, -5.9*	-31.6	35, 33*, 38*
	40	-7.4	-45.2	31
	60	-7.7	-40.4	31
	80	-6.7	-36.8	30
	100	-7.2	-41.9	19
	140	-6.5, -6.8*	-35.4	19, 22*, 20*
26-Mar-13	10	-5.0, -4.4*, -2.2*	-31.5	42, 41*, 47*
	20	-5.3	-31.4	38
	30	-4.3, -5.6*	-34.1, -32.4*	---
	40	-3.9	-24.1	43
	60	-5.6	-34.2	39
	80	-5.7	-32.0	38
	100	-5.8	-29.3, -31.8*	34
	140	-6.8, -6.2*, -6.1*	-36.5, -25.7*, -35.2*	22, 24*, 22*
30-May-13	10	-3.5, -3.3*	-16.3, -15.3*	40, 44*
	20	-4.2	-21.9	39
	30	---	---	---
	40	-5.2	-26.9	33
	60	-5.5	-25.9	30
	80	-6.6	-36.5	32
	100	-6.5	-37.6	25
	140	-6.7, -7.6*	-37.9, -40.6*	26, 31*

Table I (continued)

Date	Depth (cm)	$\delta^{18}O$ (‰)	δD (‰)	θ (%)
14-Jul-13	10	-4.4, -5.0*, -3.6*	-40.5, -38.0*, -36.2*	25, 25*, 26*
	20	-4.4	-39.6	27
	30	-5.5, -6.5*	-40.4, -27.2*	27, 26*
	40	-6.9	-40.6	23
	60	---	---	23
	80	-7.7	-39.5	24
	100	-8.0	-39.8	23
	140	-8.1, -6.3*, -5.4*	-38.7, -33.1*, -29.6*	23, 22*, 23
21-Aug-13	10	-2.0, -4.7*	-27.7, -33.5*	---
	20	-4.9	---	---
	30	---	-32.9	---
	40	-6.4	-35.9	---
	60	---	-38.6	---
	80	-7.0	-37.7	---
	100	-6.5	-35.2	---
	140	-6.8	-35.3, -18.2*	---
13-Nov-13	10	-5.8, -5.2*, -6.1*	-40.0, -33.9*, -35.6*	45, 48*, 45*
	20	---	-2.1	28
	30	-5.0, -5.9*	-36.7, -36.3*	41, 47*
	40	-5.9	-39.4	45
	60	-5.9	-38.0	41
	80	-6.0	-38.6	37
	100	-6.0	-35.5	37
	140	-5.6, -5.1*, -5.4*	-33.3, -34.3*, -33.3*	24, 23*, 26
9-Jan-14	10	-5.4, -5.1*, -5.4*	-33.9, -31.4*, -35.0*	44, 42*, 45*
	20	-6.0	-39.5	43
	30	-5.6, -5.7*	-36.5, -36.3*	45, 43*
	40	-5.7	-35.5	42
	60	-5.9	-34.9	38
	80	-5.8	-35.0	36
	100	-5.7	-32.8	37
	140	-5.6, -5.9*, -5.9*	-32.1, -32.2*, -35.0*	31, 33*, 29*
28-Feb-14	10	-5.0, -5.5*, -6.0*	-30.4, -35.7*, -38.2*	45, 45*, 44*
	20	-5.7	-35.6	44
	30	-5.4, -6.9*	-34.8, -41.6*	45, 42*
	40	-5.6	-35.5	41
	60	---	-37.4	41
	80	-5.6	-36.4	41
	100	-6.3	-37.6	38
	140	-5.6, -6.4*, -6.0*	-33.9, -34.7*, -31.5*	33, 29*, 28*

The oxygen isotope compositions of soil water samples from the microlows range from -8.1‰ to +8.2‰ with an average of -5.6 ± 1.8‰ (1σ, n = 105, figure 3A). The average $\delta^{18}O$

values of total soil water are more variable near the surface (at 10 cm, $\delta^{18}O_w$ = -4.1‰ ± 1.2, 1σ, n= 21) than at depth (at 140cm = -6.3‰ ± 0.7, 1σ, n= 20) and generally decrease with depth to an isotopic composition similar to winter precipitation (WP, figure 3A). The hydrogen isotopic compositions of distilled soil water samples from RWCMA range from -46.5‰ to -15.2‰ with a mean of -34.2‰ ± 6.1 (n = 92, figure 3B). The δD values of total soil water are more variable near the surface and generally decrease with depth from -32.1‰ ± 11.2 (at 10cm) to -36.4‰ ± 4.8 (at 140cm).

The seasonally averaged $\delta^{18}O$ profiles of vacuum distilled soil water (summer - JJA, fall - SON, winter - DJF, spring - MAM) all converge to an oxygen isotope composition that is isotopically lighter than isotopic composition of MAP ($\delta^{18}O$ range: -4.8 to -3.8‰) and similar to WP ($\delta^{18}O$ range: -6.6 to -5.5‰, figure 3C). Although the winter profile $\delta^{18}O$ values remain similar to the isotopic composition of WP from the surface to deeper portion of the soil, the other seasonal profiles (fall, summer, and spring) show larger variation throughout the profile where a general decrease in the $\delta^{18}O$ values was observed with depth in the top 60 cm and no consistent trend observed below 60 cm (figure 3C).

The gravimetric water contents of each soil sample are listed in Table 1. Water contents ranged from 16 to 57 wt. % with a mean of 30 ± 9% (1σ, n = 135). Larger variation was observed near the surface than deeper portions in the soil profile, where the mean gravimetric water contents at 10 cm and 140 cm were 36 ± 10% and 25 ± 4%, respectively (figure 3D). Gravimetric water contents during the spring, winter, and fall seasons generally decreased with depth, whereas the water content during the summer was generally lower than at other times of year and varied little with depth. The seasonally average profiles all converged to a similar water content of 25% at 140 cm (figure 3D). The $\delta^{18}O$ values of vacuum distilled soil water vary less with depth during the winter than during other seasons (Figure 3C).

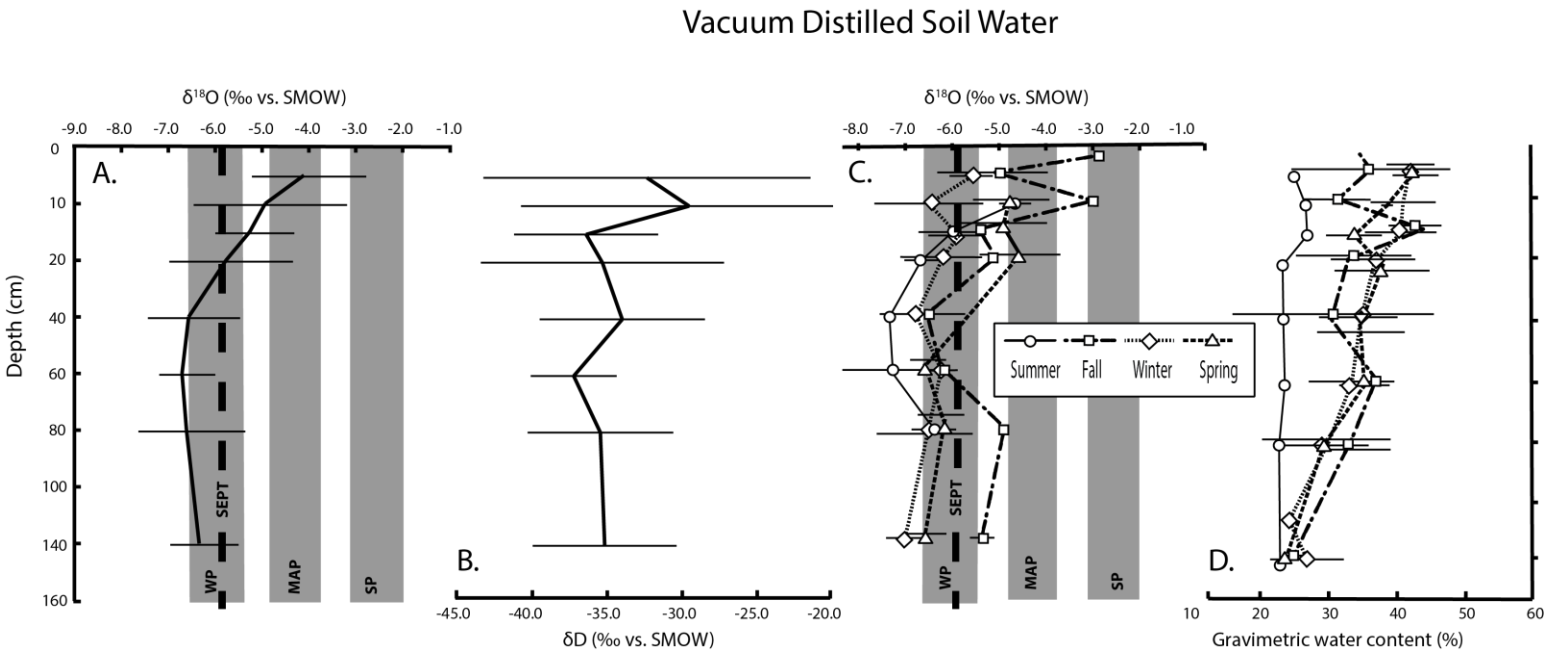

Figure 3: *Profiles of the isotopic composition and water content of vacuum distilled soil water from RCWMA. A.) The mean $\delta^{18}O$ values of soil water with depth. B.) The mean δD values of soil water with depth. C.) Seasonal means of the $\delta^{18}O$ values of total soil water. D.) Seasonal means of the gravimetric water content. Summer (June, July, and August); fall (September, October, and November); winter (December, January, and February) spring (March, April, and May) The gray boxes are the ranges between the IAEA/WMO (2013) Global Network of Isotopes in Precipitation (GNIP) and the Online Isotopes in Precipitation Calculator ((OIPC) Bowen, 2014) data sets for the different types of precipitations for Waco, TX. WP: isotopic composition of winter precipitation, MAP: isotopic composition of mean annual precipitation, SP: isotopic composition of summer precipitation, and SEPT: isotopic composition of September precipitation.*

The $\delta^{18}O$ values of vacuum distilled soil water at DB range from -5.1‰ to -2.0‰ with an average of -3.3 ± 2.2 (1σ, n = 20) (figure 4B). The $\delta^{18}O$ values were more variable near the surface than in deep portions of the soil (>80 cm) (figure 4B). The profile also converges to an isotopic composition that is isotopically lighter than the isotopic composition of MAP and similar to the isotopic composition of local WP, similar to the trend observed at RCWMA.

The oxygen isotopic compositions of vacuum distilled soil water samples from the middle and bottom of the slope at RI range from -5.1‰ to -2.0‰ with an average of -2.9 ± 1.0 (n = 13). The $\delta^{18}O$ values of vacuum distilled water collected from the bottom of the slope are isotopically heavier than the isotopic composition of MAP near the surface and generally decrease with depth to isotopic compositions similar to the isotopic composition of local MAP (figure 4C). The $\delta^{18}O$ values of vacuum distilled soil water collected in the mid-slope are consistently isotopically heavier than the isotopic composition of local MAP. The observation that vacuum distilled soil water at RI has $\delta^{18}O$ values approximately equivalent to or higher than the isotopic composition of MAP distinguishes RI from the other two sites.

4.2 The isotopic composition of soil solution sampler water, soil water in equilibrium with soil CO_2 and pedogenic carbonate

The measured $\delta^{18}O$ values of soil CO_2 and soil temperatures are listed in Table II along with the calculated $\delta^{18}O$ values of soil water in equilibrium with soil CO_2. The $\delta^{18}O$ values of water in equilibrium with soil CO_2 from RWCMA range from -4.7‰ to -2.4‰ with a mean of -3.5 ± 0.7‰ (1σ, n = 18). The mean oxygen isotope compositions of this equilibrium soil water are similar to the isotopic composition of MAP at all depths measured (figure 4A). This contrasts with the $\delta^{18}O$ values of total soil water, which decrease with depth to an isotopic composition similar to the isotopic composition of local WP and September precipitation. Additionally, the $\delta^{18}O$ values of soil water from the solution sampler average -4.5 ± 0.2‰, which is similar to the isotopic composition of MAP (-4.5 ± 0.2‰). The isotopic composition of the deep soil water (> 80 cm) determined by the four methods (vacuum distillation, equilibrium with CO_2, solution sampler, equilibrium with pedogenic carbonate) are shown versus time in figure 5B. The $\delta^{18}O$ values of soil water in equilibrium with CO_2 and that collected from the solution sampler are indistinguishable from each other and similar to the isotopic composition of MAP throughout the study interval. In contrast, the $\delta^{18}O$ values of the vacuum distilled sample remain similar to or

lower than the isotopic composition of WP. Additionally, the differences between the mean $\delta^{18}O$ values of deep soil water in equilibrium with soil CO_2 and soil water from vacuum distillation are larger during the summer and smaller during the winter.

The calculated oxygen isotope compositions of soil water in equilibrium with soil CO_2 at the Dance Bayou site range from -3.4‰ to -1.8‰ with an average of -2.4 ± 0.6 (n = 7). The soil water in equilibrium with soil CO_2 does not show a trend with depth and is isotopically similar to or heavier than the isotopic composition of MAP (figure 4B). This contrasts with the $\delta^{18}O$ values of vacuum distilled soil water, which decrease with depth to an isotopic composition similar to the isotopic composition of local WP. The calculated oxygen isotopic composition of water in equilibrium with CO_2 from RI ranges from -4.4‰ to -2.7‰ with an average of -3.6 ± 0.8 (n = 4) and no trend with depth (figure 4C). In contrast to RCWMA and DB, the isotopic compositions of soil water in equilibrium with soil CO_2 and distilled soil water are similar to each other and to the isotopic composition of MAP.

The measured $\delta^{18}O$ values (vs. VPDB) of soil carbonate nodules at RWCMA, RI, and DB were -4.0 ± 0.2‰ (n = 2), -3.4 ± 0.3‰ and -3.3 ± 0.2‰ (n = 6), respectively. Deep soil temperatures measured at RCWMA range from 16.0°C to 25.7°C with an average of 19.5 ± 2.8°C. This temperature range was used to calculate a range of $\delta^{18}O$ values of water in equilibrium with calcite. A temperature range of 10 to 29 °C was used for RI and 15 to 25 °C for DB. Using temperature ranges and the calibration of Romanek (1992), the calculated $\delta^{18}O$ ranges (vs. SMOW) for soil water in equilibrium with pedogenic carbonate for RWCMA, RI, and DB were calculated (-3.4‰ to -1.4‰, -4.2‰ to -0.2‰, and -2.9‰ to -0.9‰, respectively, Table II). The isotopic compositions of soil water in equilibrium with pedogenic carbonate at the three field sites are isotopically heavier than the isotopic composition of MAP and generally similar to SP (figure 4).

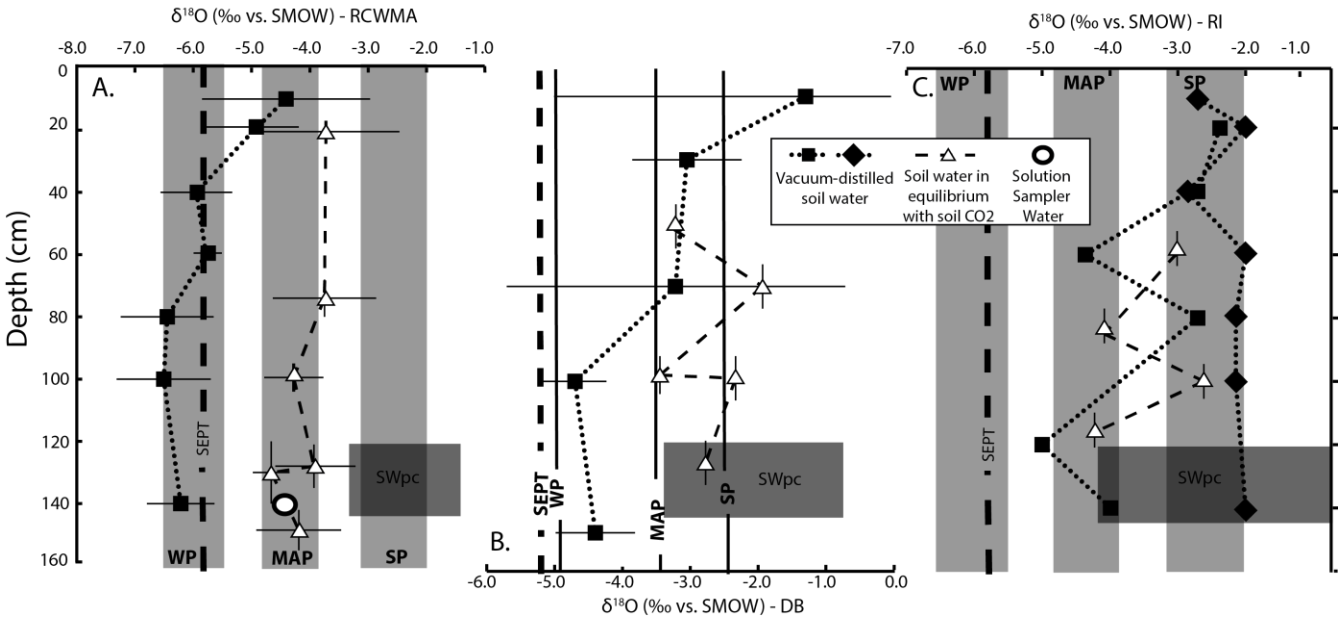

Figure 4*: Comparison between $\delta^{18}O$ values of soil water obtain through cryogenic vacuum distillation (black squares, microlows only), soil water collected from solution sampler (open circle), and soil water in equilibrium with soil CO_2 (open triangles) and pedogenic carbonate (dark gray boxes). A. The $\delta^{18}O$ values of the four different soil waters at RCWMA. B. The $\delta^{18}O$ values of three different soil waters (excluding water from the solution sampler) at DB. C. The $\delta^{18}O$ values of three different soil waters (excluding water from the solution sampler) at RI. Profiles were collected from the down-slope (black squares) and mid-slope (black diamonds) at RI. The isotopic composition of different precipitation for DB was obtained from OIPC. The gray boxes are the $\delta^{18}O$ ranges between GNIP and OIPC data for Waco, TX precipitation. The dark gray boxes are the calculated $\delta^{18}O$ values of soil water in equilibrium with pedogenic carbonate based on a temperature range at that site. SWpc: Soil water in equilibrium with pedogenic carbonate. WP: isotopic composition of winter precipitation, MAP: isotopic composition of mean annual precipitation, SP: isotopic composition of summer precipitation, and SEPT: isotopic composition of September precipitation.*

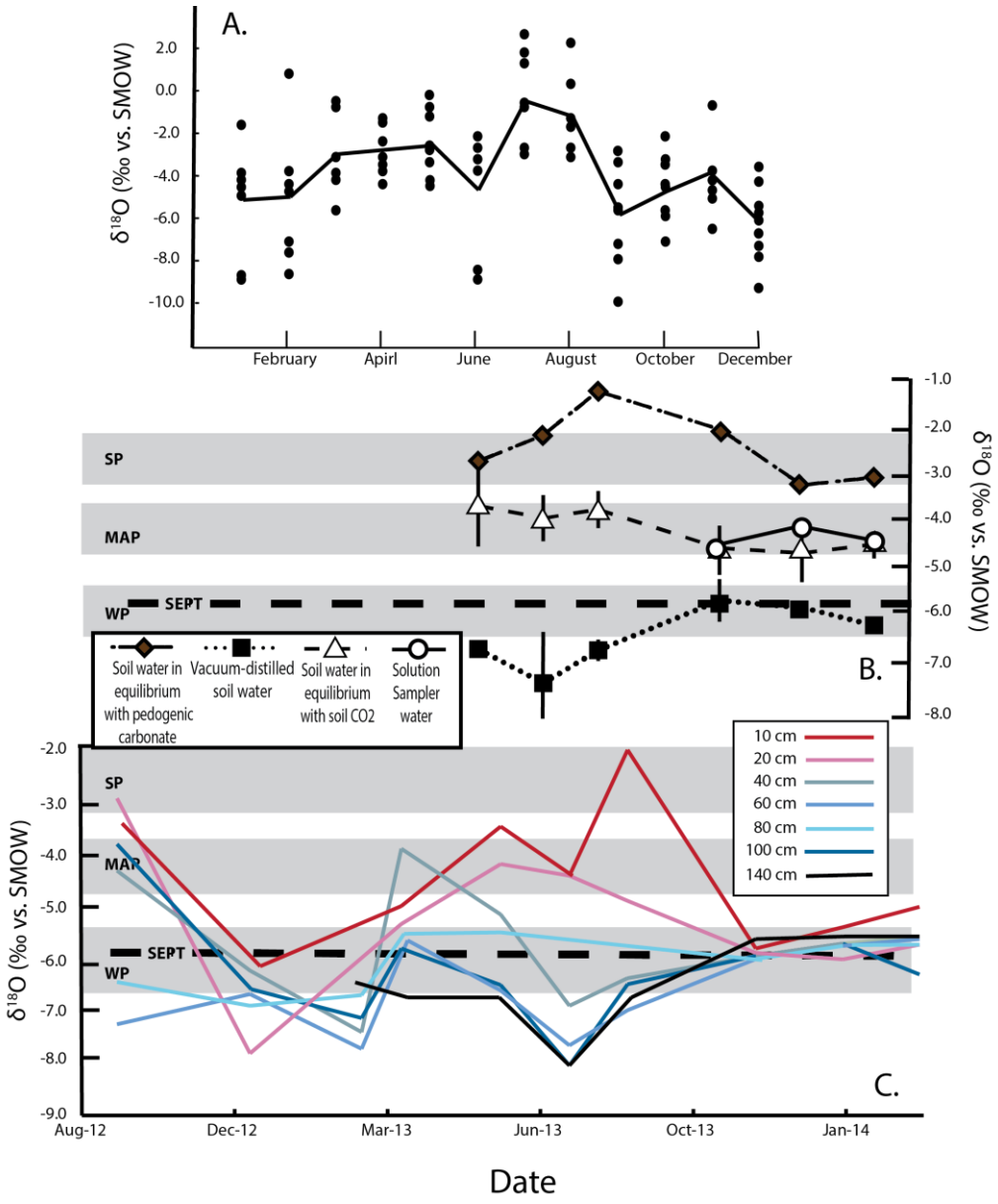

Figure 5*: The seasonal variation in the isotopic composition of soil water and precipitation at RCWMA. A. The $\delta^{18}O$ value of precipitation from the GNIP data set (black dots) and the $\delta^{18}O$ mean for each month (black line). B. The seasonal variation of deep (>80cm) total soil water (black squares), deep soil water in equilibrium with CO_2 (open triangles), soil water collected from the solution sampler (open circles), and deep soil water in equilibrium with pedogenic carbonate (black diamonds). C. The seasonal variation in the $\delta^{18}O$ values of soil water at each sampling depth. The gray boxes are the ranges between GNIP and OIPC data sets for Waco, TX precipitation. summer (June, July, and August); fall (September, October, and November); winter (December, January, and February) spring (March, April, and May) WP: isotopic composition of winter precipitation, MAP: isotopic composition of mean annual precipitation, SP: isotopic composition of summer precipitation, and SEPT: isotopic composition of September precipitation.*

***Table II**: The $\delta^{18}O$ values of soil CO_2 and soil water in equilibrium with CO_2, including the soil temperature during sampling at RCWMA. (*) soil temperatures on May 30, 2013 were calculated by interpolation from temperature measured in April 28, 2013 and July 14, 2013. (`) Soil temperatures for well LA 10 were calculated from the temperature mean of well LC 95, LD 113, and LE 135.*

	$\delta^{18}O_{soil\ CO2}$ (‰ vs. VPDB)	Soil Temp. (°C)	$\delta^{18}Osw_{CO2}$ (‰ vs. SMOW)	$\delta^{18}Osw_{pc}$ (‰ vs. SMOW)
Date	*LD 17 (17-24cm)*			
8-Sep-12	---	25.8	---	---
11-Nov-12	---	19.4	---	---
11-Dec-12	---	15.3	---	---
22-Jan-13	---	12	---	---
27-Feb-13	---	12.8	---	---
26-Mar-13	---	14	---	---
28-Apr-13	---	18.1	---	---
30-May-13	8.4	21.3*	-2.5	---
20-Jun-13	7.4	23.3	-2.8	---
14-Jul-13	7.1	24.6	-2.6	---
21-Aug-13	---	26.9	---	---
13-Nov-13	6.3	16.6	-5.6	---
9-Jan-14	8.8	10.4	-4.6	---
28-Feb-14	8.4	13.8	-4.2	---
	LD 60 (68-80cm)			
8-Sep-12	---	25	---	---
11-Nov-12	---	19.9	---	---
11-Dec-12	---	18.7	---	---
22-Jan-13	---	14	---	---
27-Feb-13	---	14.8	---	---
26-Mar-13	---	16.1	---	---
28-Apr-13	---	17.5	---	---
30-May-13	8.8	19.9*	-2.4	---
20-Jun-13	7.3	21.5	-3.2	---
14-Jul-13	6.3	23.1	-3.5	---
21-Aug-13	---	26.3	---	---
13-Nov-13	6.3	20	-4.8	---
9-Jan-14	8.4	13.5	-4.2	---
28-Feb-14	7.8	15.8	-4.3	---

Table II (continued)

	$\delta^{18}O_{soil\ CO2}$ (‰ vs. VPDB)	Soil Temp. (°C)	$\delta^{18}Osw_{CO2}$ (‰ vs. SMOW)	$\delta^{18}Osw_{pc}$ (‰ vs. SMOW)
Date	*LC 95 (95-104cm)*			
8-Sep-12	---	24.4	---	---
11-Nov-12	---	20.3	---	---
11-Dec-12	---	19.1	---	---
22-Jan-13	---	15.2	---	---
27-Feb-13	---	15	---	---
26-Mar-13	---	14.6	---	---
28-Apr-13	---	16.8	---	---
30-May-13	7.3	18.0*	-4.3	---
20-Jun-13	6.7	18.8	-3.9	---
14-Jul-13	6.3	22.5	-3.8	---
21-Aug-13	---	25.1	---	---
13-Nov-13	6.8	22.1	-3.9	---
9-Jan-14	7.3	14.8	-5.0	---
28-Feb-14	7.4	15.5	-4.7	---
	LD 113 (121-135cm)			
8-Sep-12	---	23.7	---	-1.8
11-Nov-12	---	20.9	---	-2.4
11-Dec-12	---	19.2	---	-2.8
22-Jan-13	---	16.3	---	-3.4
27-Feb-13	---	16	---	-3.5
26-Mar-13	---	16.5	---	-3.3
28-Apr-13	---	17.1	---	-3.2
30-May-13	8.7	18.6*	-2.8	-2.9
20-Jun-13	7.1	19.6	-3.7	-2.7
14-Jul-13	6.0	21.7	-4.0	-2.3
21-Aug-13	---	25.7	---	-1.4
13-Nov-13	5.8	21.7	-4.9	-2.3
9-Jan-14	8.1	16.3	-3.9	-3.4
28-Feb-14	7.5	17.1	-4.3	-3.2

Table II (continued)

	$\delta^{18}O_{soil\ CO2}$ (‰ vs. VPDB)	Soil Temp. (°C)	$\delta^{18}Osw_{CO2}$ (‰ vs. SMOW)	$\delta^{18}Osw_{pc}$ (‰ vs. SMOW)
Date	*LE 135 (142-155cm)*			
8-Sep-12	---	23.3	---	-1.9
11-Nov-12	---	21.4	---	-2.3
11-Dec-12	---	20.6	---	-2.5
22-Jan-13	---	17.5	---	-3.1
27-Feb-13	---	16.0	---	-3.5
26-Mar-13	---	16.9	---	-3.3
28-Apr-13	---	18.0	---	-3.0
30-May-13	7.9	19.0*	-3.5	-2.8
20-Jun-13	7.2	19.6	-3.8	-2.7
14-Jul-13	6.7	21.0	-3.4	-2.4
21-Aug-13	---	25.1	---	-1.6
13-Nov-13	5.9	21.9	-4.8	-2.2
9-Jan-14	7.0	16.9	-4.9	-3.3
28-Feb-14	7.0	17.0	-4.8	-3.2
	LA 120 (120-140cm)			
8-Sep-12	---	**23.8`**	---	-1.8
11-Nov-12	---	**20.9`**	---	-2.4
11-Dec-12	---	**19.6`**	---	-2.7
22-Jan-13	---	**16.3`**	---	-3.4
27-Feb-13	---	**15.7`**	---	-3.5
26-Mar-13	---	**16.0`**	---	-3.5
28-Apr-13	---	**17.3`**	---	-3.2
30-May-13	7.0	**18.5`**	-4.5	-2.9
20-Jun-13	6.1	**19.3`**	-4.7	-2.7
14-Jul-13	5.8	**21.7`**	-4.3	-2.2
21-Aug-13	---	**25.3`**	---	-1.5
13-Nov-13	5.8	**21.9`**	-4.9	-2.2
9-Jan-14	6.9	**16.0`**	-5.1	-3.5
28-Feb-14	7.5	**16.5`**	-4.5	-3.3

4.3 The isotopic composition of precipitation

The isotopic compositions of monthly precipitation for Waco, TX used in this study were obtained from the IAEA/WMO (2013) Global Network of Isotopes in Precipitation data set (http://nucleus.iaea.org/CIR/CIR/GNIPIHIS.html). The dataset spans from 1962-1965 and from 1972-1976 for a total of 7 years. RCWMA and RI are within 98 and 28 km of Waco, respectively. The isotopic compositions of mean annual and seasonal precipitation for all three sites were calculated using the Online Isotope in Precipitation Calculator (OIPC, Bowen, 2014). The $\delta^{18}O$ values of soil water was also compared to the $\delta^{18}O$ values of precipitation reported in Pape et al. (2010), which reported more recent precipitation from a father location from our field site (Austin, TX).

The $\delta^{18}O$ values of monthly Waco rainwater samples between 1962 and 1976 range from -9.9‰ to 2.7‰ with a weighted-mean of -3.8 ± 2.7 (1σ, n = 96). Four samples of RWCMA rainwater were collected from December 2012 to July 2013, with $\delta^{18}O$ values ranging from -5.0‰ to 0.2‰ with an average of -2.7 ± 2.2. The oxygen isotope composition of Waco precipitation shows no correlation with either temperature or precipitation amount ($R^2 = 0.0124$) (figure A10), and when RWCMA precipitation $\delta^{18}O$ values are compared with average temperature during each collection interval, no correlation was observed either ($R^2 = 0.0009$) (figure A11). Despite the lack of correlation with surface temperature and precipitation amount, the oxygen isotopic composition of RCWMA rainwater shows seasonal variation, with isotopically lighter values measured during the winter (mean $\delta^{18}O$ = -5.5 ± 2.4) than the summer season (JJA, mean $\delta^{18}O$ = -2.0 ± 2.9, figure 5A). The δD values of Waco rainwater samples (GNIP) range from -58.9‰ to 18.0‰ with an average of -19.9 ± 18.2. The δD values RWCMA rainwater samples range from -40.8‰ to 2.3‰ with an average of -15.2 ± 22.7.

The equation for the local meteoric water line (LMWL) for Waco, TX, based on the GNIP data and the LMWL for Austin, TX (Pape et al., 2010) is $y = 6.5x + 4.6$ ($R^2 = 0.9$) and $y = 7.1x + 6.7$ ($R^2 = 0.9$) (figure 6). Most total soil water analyses from RCWMA are lighter than the isotopic composition of MAP and generally plot on the lower (isotopically lighter) end of the Waco LMWL (figure 6). When compared to Austin LMWL, total soil water generally plots

more lower on the line than observed when plotted on the Waco LMWL. Deviations in $\delta^{18}O$ from the Waco LMWL were calculated in this study rather than *d*-excess values because the $\delta^{18}O$ deviations directly relate to the LMWL (i.e., positive values plot to the right of the Waco LMWL and negative values to the left) and therefore facilitate interpretation. The $\delta^{18}O$ deviation from the Waco LMWL of samples near the surface (<50 cm) is more variable than the samples collected deeper in the soil profile (>50 cm) (figure 7B). The $\delta^{18}O$ deviations from the Waco LMWL of the shallower samples (<50 cm) generally plot on the right side of the Waco LMWL (i.e., isotopically heavier than LMWL), whereas deeper samples (>50 cm) generally plot to the left side of the Waco LMWL (figure 7B). Vacuum distilled soil water samples collected during the spring and winter generally plot closer to the LMWL than do samples collected during the summer and fall samples. A positive correlation was observed between $\delta^{18}O$ values and $\delta^{18}O$ deviations from the Waco LMWL for summer and fall, but not for winter and spring samples (figure 7A).

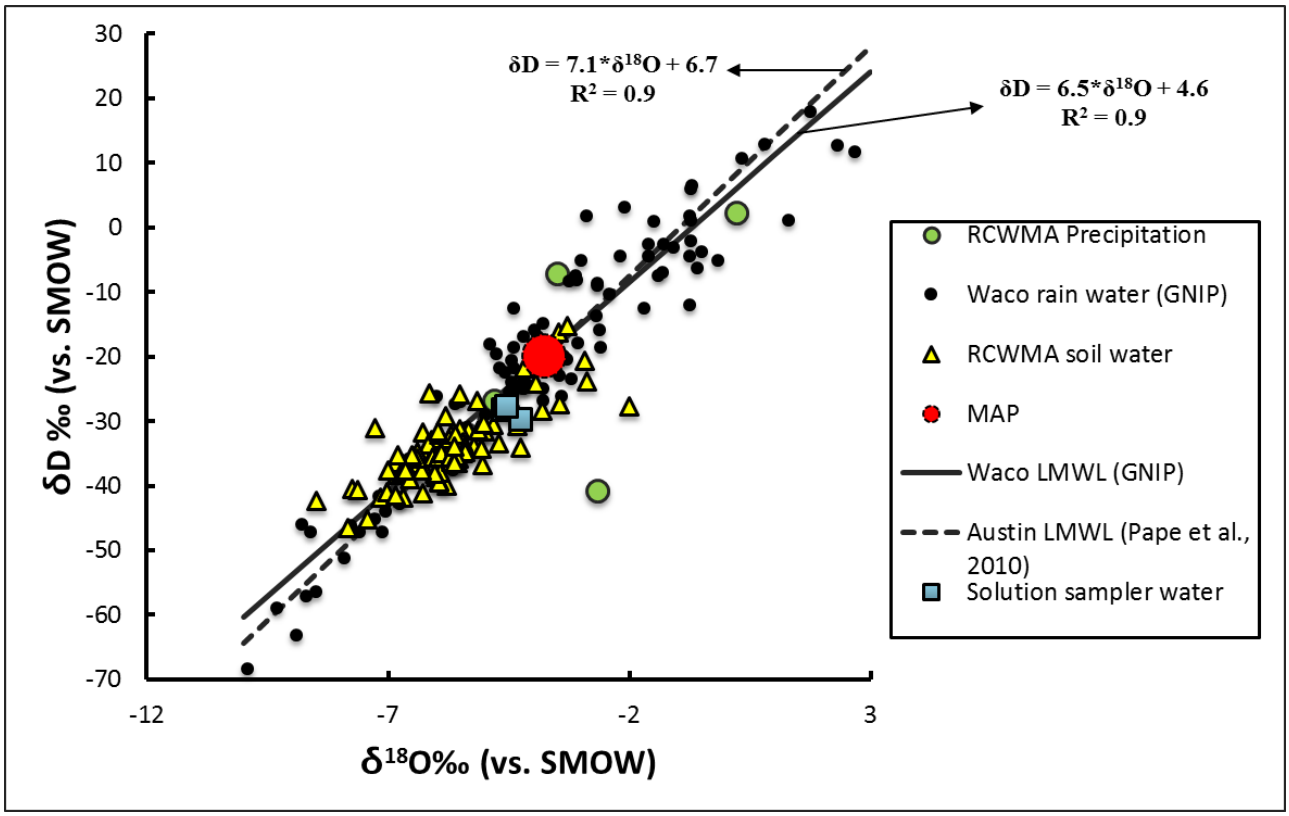

Figure 6*: The Meteoric Water Line of Waco, Texas (black line) from rain water from GNIP, the Meteoric Water Line of Austin, TX (black dash line) from Pape et al. (2010), distilled soil water (yellow triangles), water collected from the solution sampler (blue squares), collect rainwater from RCWMA (green dots) and the isotopic composition of local mean annual precipitation in Waco, TX (large red dot). All soil water points plot on or near the LMWL which suggest that they are all rainwater and have not been subjected to any kinetic process that would cause fractionation, such as evaporation. However, the soil water samples generally plot on the lighter side of the two LMWL (isotopically lighter than the isotopic composition of MAP).*

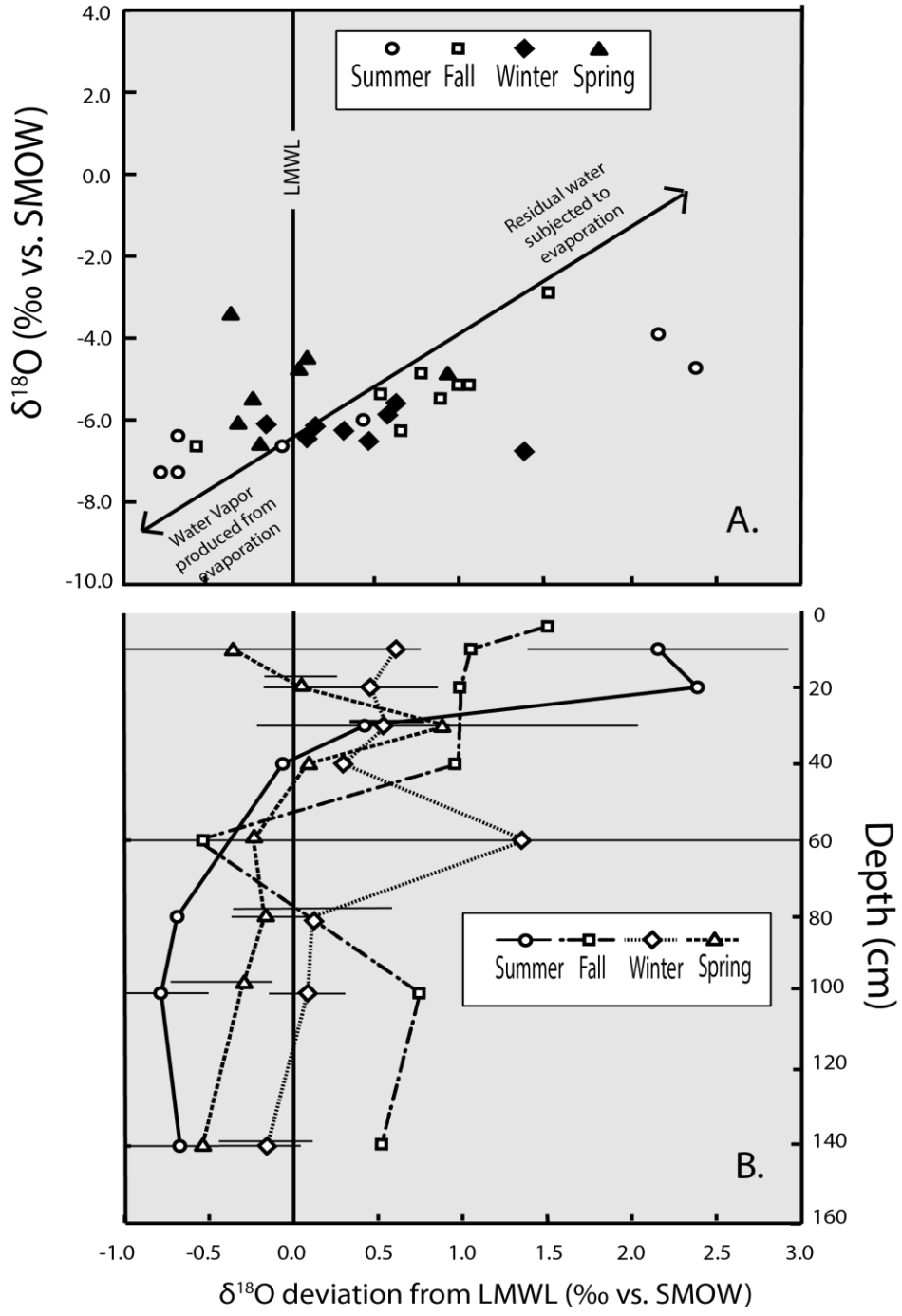

Figure 7: *(A.) $\delta^{18}O$ values and (B.) Depth plotted against the $\delta^{18}O$ deviation from the LMWL for samples from RCWMA. summer (June, July, and August); fall (September, October, and November); winter (December, January, and February) spring (March, April, and May)*

Chapter 5: Discussion

5.1 Isotopically distinct pools of water in Vertisols

Comparing the oxygen isotope compositions of vacuum distilled soil water, water from the soil solution sampler, and soil water in equilibrium with CO_2 and pedogenic carbonate suggest that these methods sample different fractions of total soil water. The vacuum distilled method collected total soil water, which is a mixture of immobile (micropore) and mobile (macropore) water, whereas the soil solution sampler collected predominantly mobile (macropore), gravitational water (Landon et al., 1999; Zhao et al., 2013). The calculated oxygen isotope composition of soil water in equilibrium with soil CO_2 was indistinguishable from water collected by the soil solution sampler, which suggests that CO_2 equilibrates with mobile water in the soil, despite the fact that immobile soil water may dominate the water pool, especially during the summer. In the Vertisols at RCWMA and DB, we measured consistently higher $\delta^{18}O$ values in the mobile water versus the immobile water. However, at RI, the isotopic composition of soil water in equilibrium with CO_2 and total water were similar, suggesting that the immobile and mobile water are readily mixing with each other.

5.2 Processes affecting the isotopic composition of soil water in Vertisols

The average oxygen isotope profile for all vacuum distilled samples from RCWMA illustrates more variation near ground surface, where soil water is subject to evaporation and precipitation events that vary seasonally in isotopic composition. However, the smaller variations in soil water sampled from deeper in the profile suggests either that water from different precipitation events is well mixed by the time it percolates to deep soil or that only certain precipitation events with similar isotope compositions recharge the deep soil. The mean seasonal oxygen isotope profiles of vacuum distilled soil water from RCWMA converging to an isotopic composition similar to that of the isotopic composition of local WP and September precipitation, suggesting a deep reservoir of winter and/or September precipitation that does not change isotopically throughout the year. Additionally, the isotopic composition of distilled soil water from RCWMA plotted lower than the isotopic composition of MAP on the LMWL, which suggests that total soil is biased towards WP (figure 6).

Brooks et al. (2010) suggest that precipitation events that rewet dry soil after the summer control the isotope composition of immobile water. In their study area, individual events with progressively lighter precipitation rates through time occur at the end of summer/beginning of fall. These storms result in progressively decreasing $\delta^{18}O$ values in immobile water with depth, because percolating rain continually bypasses previous rain in the soil (figure 8A). Isotopically light precipitation at the end of summer/beginning of fall (September precipitation) occurs in Waco as well (figure 5A). Because Vertisols are typically extremely dry and cracked in September, these isotopically light events might recharge the deep soil, especially if localized surface runoff routes water into these cracks. After the soils seal up with increasing water content, periods of ponding and low ET might also occur causing the water to have a longer residence time in the soil (figure 8B). Therefore, our data from RCWMA and DB are consistent with September precipitation being the source for deep total (mobile) soil water; however, our data are also consistent with contributions of winter precipitation to deep soil water. Our observation differ from Gazis (2004), where they concluded that the isotopic composition of deep soil water is similar to that of the isotopic composition of MAP because deep soil water is a mixed reservoir of rain events occurring throughout the year.

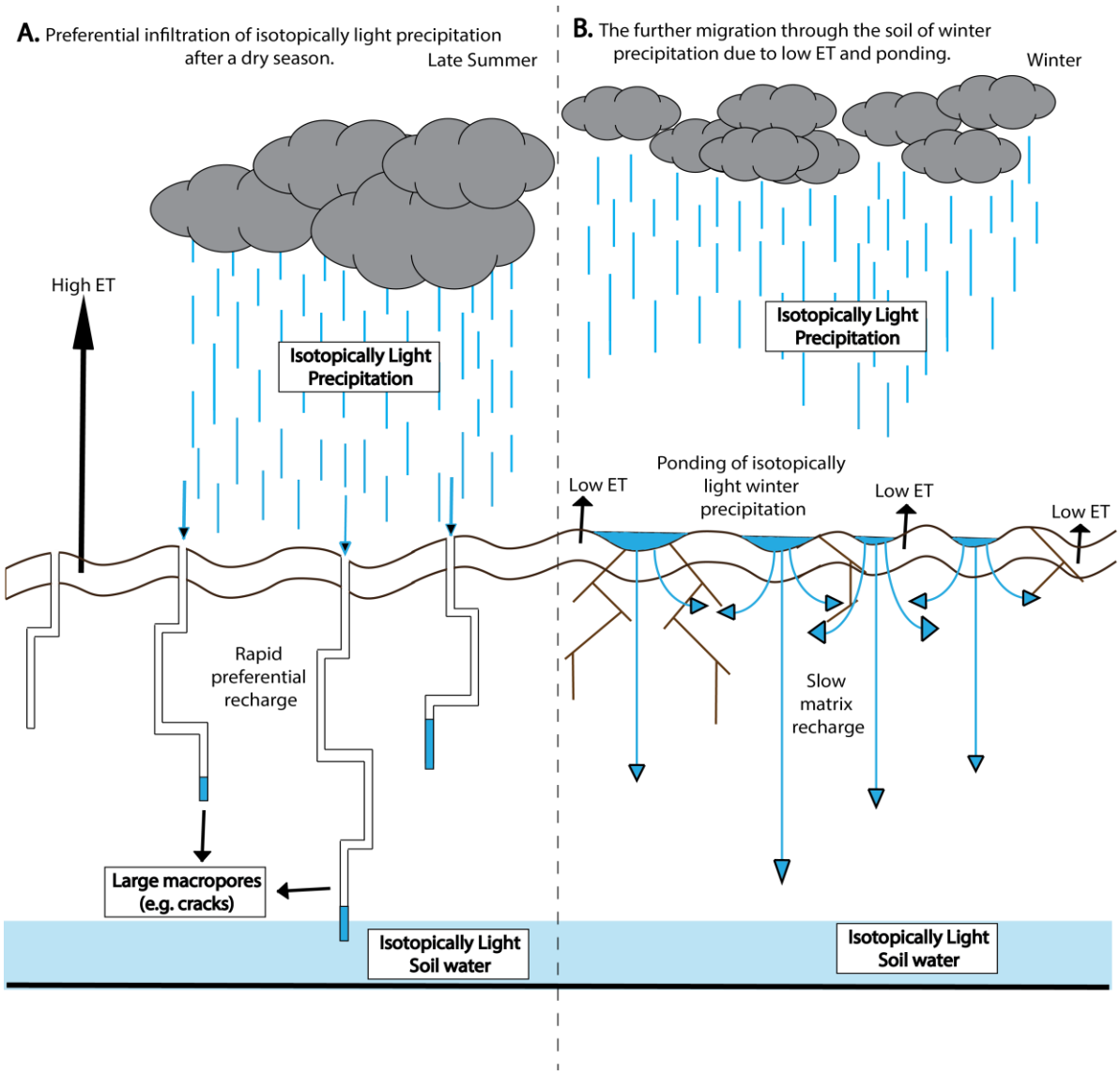

***Figure 8**: Two conceptual models to explain isotopically light deep soil water Vertisols at RCWMA. (A) The preferential infiltration of isotopically light precipitation from large rain events following the dry seasons. This idea suggests that late summer events that recharges deep soil water are from large rain events. (B) The recharge of isotopically light winter precipitation in the soil due to low ET and ponding (due to saturated soil). This idea is different from preferential infiltration of large rain events in late summer because all the rain during the winter season mixes with each other before recharge of deep soil.*

Deep total soil water at RI has an isotopic composition similar to or heavier than the isotopic composition of MAP. This might be explained by the different geomorphic setting of RI, versus RCWMA and DB soils, both of which exist on floodplains and therefore have different hydrological properties than the hillslope at RI. Perhaps the isotopically light precipitation that controls deep total soil water (as seen at RCWMA and DB) tends to run off the hillslope at RI rather than infiltrating, leaving the deep total soil water closer in isotopic composition to MAP or SP. Precipitation is isotopically lighter during the winter season. Wet soil during the winter season results in slow infiltration rates causing more runoff of winter rain from hill slopes to the bottom of the hill. Preferential runoff of isotopically light precipitation is generally consistent with the lower $\delta^{18}O$ values of total soil water at the bottom of the slope which receives run on. In this case, September precipitation is not one of the sources for the isotopically light deep soil water because the September rain would infiltrate even on the hill slope through large cracks at that time of year (Arnold et al., 2005) causing the isotopic composition of deep soil water on the hill slope to be lighter, but this is not observed in our data.

It is also possible that differences in vegetation among the sites explain this discrepancy. One possibility is that large trees remove a great amount of deep soil water and micropores during the summer, which then can be refilled with isotopically light winter and/or September precipitation. However, in the grassland at RI, the water content of the deep soil water does not vary much throughout the year (Breecker et al 2013) allowing water in micropores to consistently exchange with water in macropores.

The $\delta^{18}O$ value of the mobile water is similar to or heavier than the isotopic composition of MAP, which is consistent with either evaporation of water with an isotopic composition of MAP or a bias toward SP (figure 4A) (Gazis, 2004). The isotopic compositions of mobile water are consistently heavy throughout the year and were not light enough to justify the presence of immobile water (figure 5B).

Deviations of $\delta^{18}O$ in total soil water from LWML for RCWMA samples collected at 140 cm depth generally plot on or to the left of the LMWL, which suggest that these samples were sourced by precipitation and were not subjected to evaporation. Deep evaporation was hypothesized to occur in Vertisols during warm (summer) seasons when cracks penetrate deeply into the soil. Evaporation can be evaluated by comparing soil waters with the LMWL. Most of

our soil water results plot on the LMWL of Waco, Texas and this suggests they were sourced by precipitation that have not been subjected to evaporation in the soil. However, the isotopically heaviest samples, which were collected in the summer/fall season and near the surface (<50 cm), deviate furthest to the right of the LMWL (figure 7A), suggesting that these samples have been subjected to evaporation. The opposite can be observed and stated for the samples with the lowest $\delta^{18}O$ values, which plot to the left of the LMWL, consistent with the isotopic composition of vapor resulting from kinetic isotope fractionation during evaporation. An influence of downward vapor flux on the isotopic composition of immobile water seems unlikely in this sub-humid climate, but it is consistent with the data and the possible magnitude of this effect should be evaluated in the future.

We considered the potential for fractionation due to adsorption of soil water to clay surfaces, which was observed in Coplen and Hanshaw (1973) and Oerter (2013). Based on their findings, the direction of the fractionation (mobile water becoming isotopically light or heavy) depends on the type of montmorillonite within the soil, potentially explaining deep soil water that is isotopically light. Fractionation due to adsorption follows the Rayleigh curve (figure 13A), where the immobile water gradually becomes isotopically lighter or heavier with depth depending on the direction of fractionation. However, in our case, we observed that immobile water becomes lighter to a certain depth and then no longer changes with depth, which does not follow the Rayleigh curve. With future investigation, fractionation due to adsorption could be a plausible process to explain why mobile water is never light enough to explain immobile water.

5.3 Pedogenic carbonate recording mobile water

Our result showed that the oxygen isotope composition of soil water in equilibrium with pedogenic carbonate is isotopically heavier than both mobile and immobile water, but more similar to that of mobile water. This suggests that pedogenic carbonate records the isotopic composition of mobile water that has been subjected to evaporation and/or sourced from SP. We did not observe such high $\delta^{18}O$ values in mobile water during the interval of study, but evaporation of the deep, mobile water pool is plausible during the droughts when pedogenic carbonate may form. Because mobile water exists mainly in macropores, this also suggests that pedogenic carbonates may form in macropores in the Vertisols studied, where large shrink/swell driven macropore pCO_2 fluctuations have been recorded (Breecker et al., 2013) (figure 9).

Indeed, the occurrence of large horizontal pCO_2 variability as Vertisols dry and crack suggests that micropores may maintain high CO_2 concentrations (several % CO_2), preventing calcium carbonate precipitation, even as macropore CO_2 decreases to near atmospheric levels (Breecker et al., 2013).

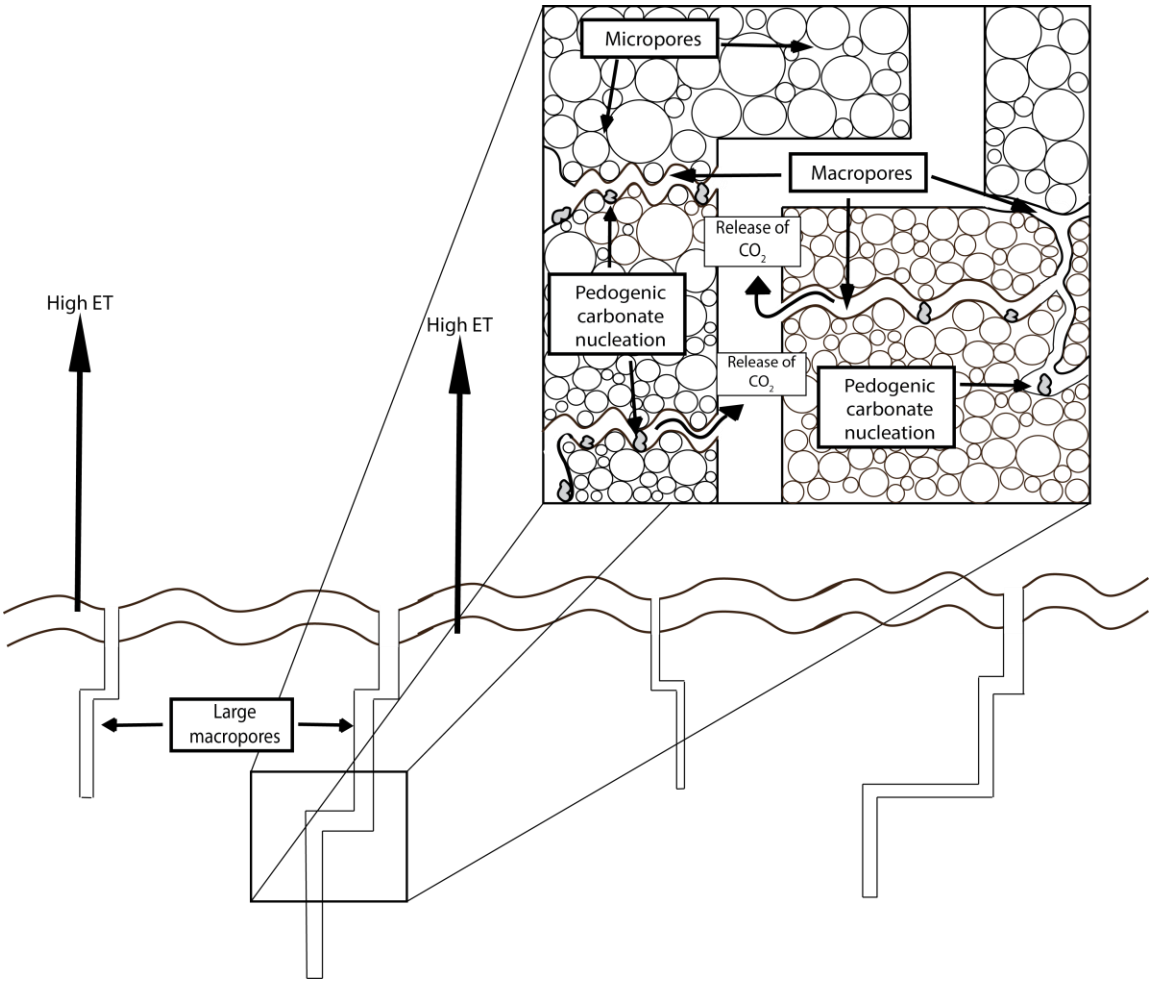

Figure 9: *A model illustrating the precipitation of pedogenic carbonate in the macropores of the soil. Macropores are the large openings in the soil where water (mobile water) is under gravitational flow. Micropores are the water that is tightly bounded to soil grains and in between grains that is under matrix flow, which include diffusive processes. Degassing of soil CO_2 from the soil induces the precipitation of pedogenic carbonate. The isotopic composition of pedogenic carbonate recording mobile water suggest that they form in macropores, not micropores, as illustrated in the figure above.*

If pedogenic carbonates do provide a record of the $\delta^{18}O$ values of mobile water, then the δD values of leaf wax n-alkanes, which may be sourced from the immobile water used by plants (Brooks et al. 2010), may provide a complementary insight into paleohydrology. For instance, the available data from seasonally dry climates, in which pedogenic carbonate typically forms, suggest that leaf waxes may record precipitation during those events that wet the soil following the dry season, whereas pedogenic carbonates may record summer precipitation (e.g. Hough et al., 2014).

Chapter 6: Conclusion

Due to the complex hydrology of the Vertisols examined in this research, many processes can affect the isotopic composition of soil water, causing different pools of the total soil water to be isotopically distinct. The isotopic composition of deep total water may be controlled by preferential recharge of deeper soil by isotopically light precipitation in September and/or the winter precipitation during saturated conditions and low ET. The isotopic composition of soil water in equilibrium with soil CO_2 and solution sampler water are indistinguishable; therefore, the isotopic composition of soil CO_2 records mobile water in macropores. Lastly, the isotopic composition of soil water in equilibrium with pedogenic carbonate is isotopically heavier than the isotopic composition of MAP, but similar to the isotopic composition of SP, suggesting that pedogenic carbonate in these soils may record the isotopic composition of mobile water influenced by evaporation and/or SP and may form in macropores rather than micropores. This could have important implications for climate models used to reconstruct past climate because the different processes that that leads these bias signatures of SP recorded by pedogenic carbonate would need to be incorporated into the models for more accurate results. Additionally, the bias recording of SP and/or evaporated oxygen isotope compositions needs to be take into account when paleosol carbonates isotopic composition is compared to modern climate to reconstruct paleoclimate.

Appendix: Figures

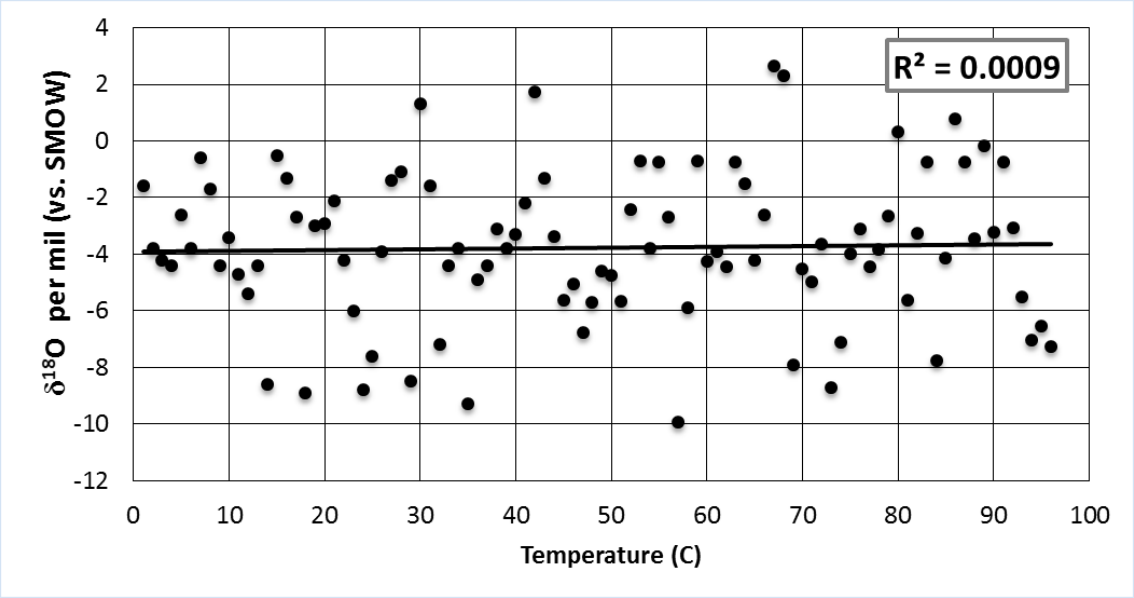

***Figure 10**: The $\delta^{18}O$ values of rain water (GNIP) (black dots) with temperature. No correlation was observed*

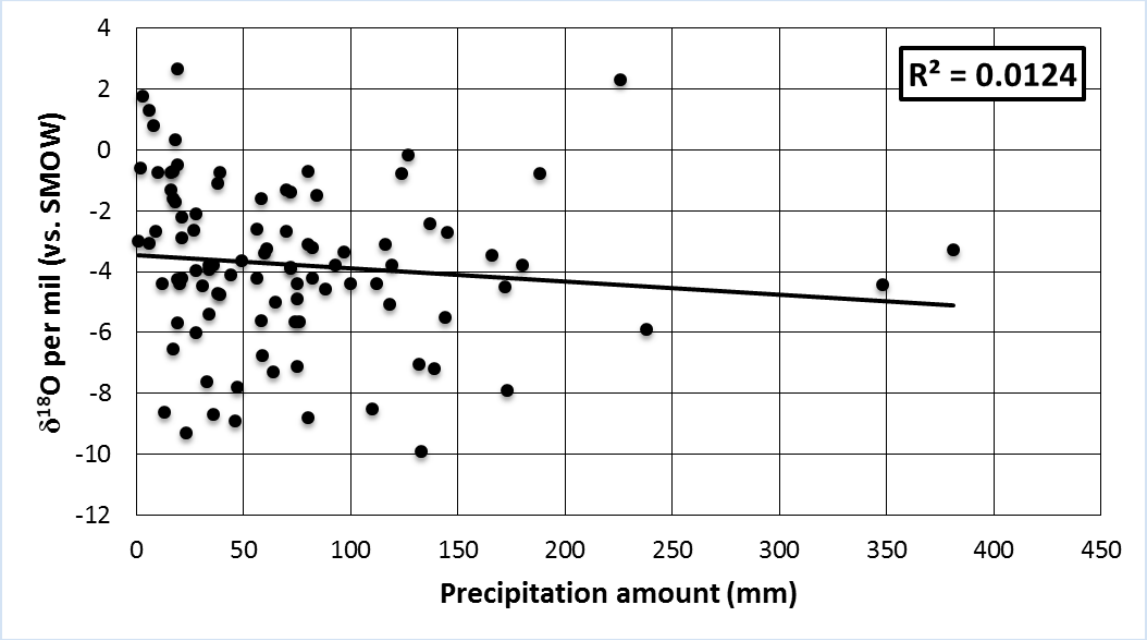

***Figure 11**: The $\delta^{18}O$ values of rain water (GNIP) (black dots) with precipitation amount. No correlation was observed*

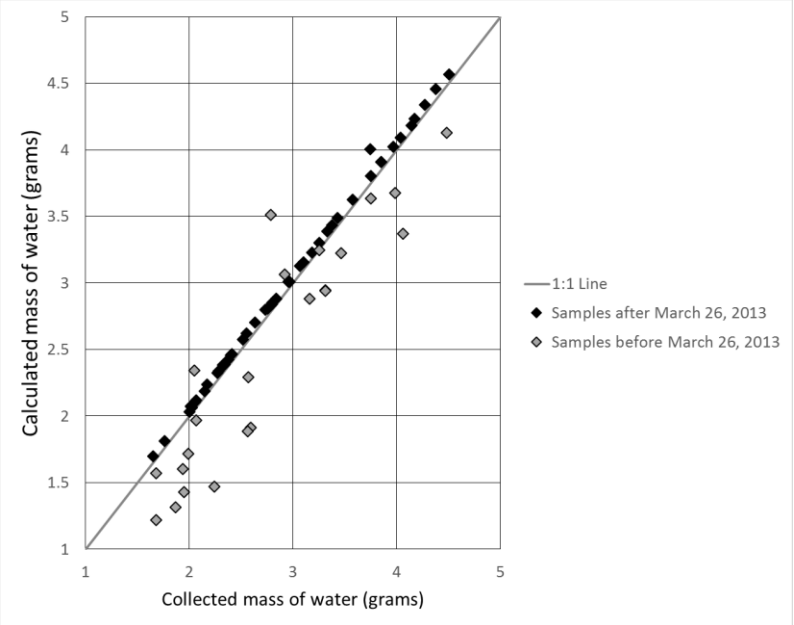

Figure 12: *The 1:1 line for the mass (in grams) of the soil water collected after vacuum distillation and the calculated mass obtained by subtracting the mass of the before and after the extraction. Samples collected before March 26, 2013 are not closely correlated with each other because water from the atmosphere was pulled into dry soil samples left open to the atmosphere after extraction. Therefore, the mass of collected water was high than that of the calculated water mass.*

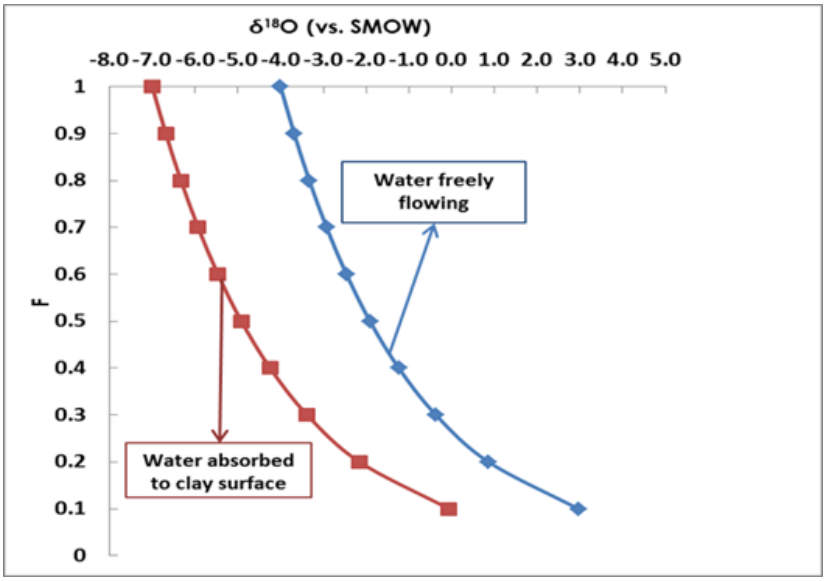

Figure 13: *Fractionation due to adsorption of water to clay surfaces as the water percolates through the soil. The isotopic composition of mobile water will become isotopically heavier as isotopically light water is adsorbed to clay surfaces during percolation (blue line). Additionally, as more isotopically light water adsorbs to clay surfaces, the following water to adsorb to clay surfaces will be isotopically heavier (red line).*

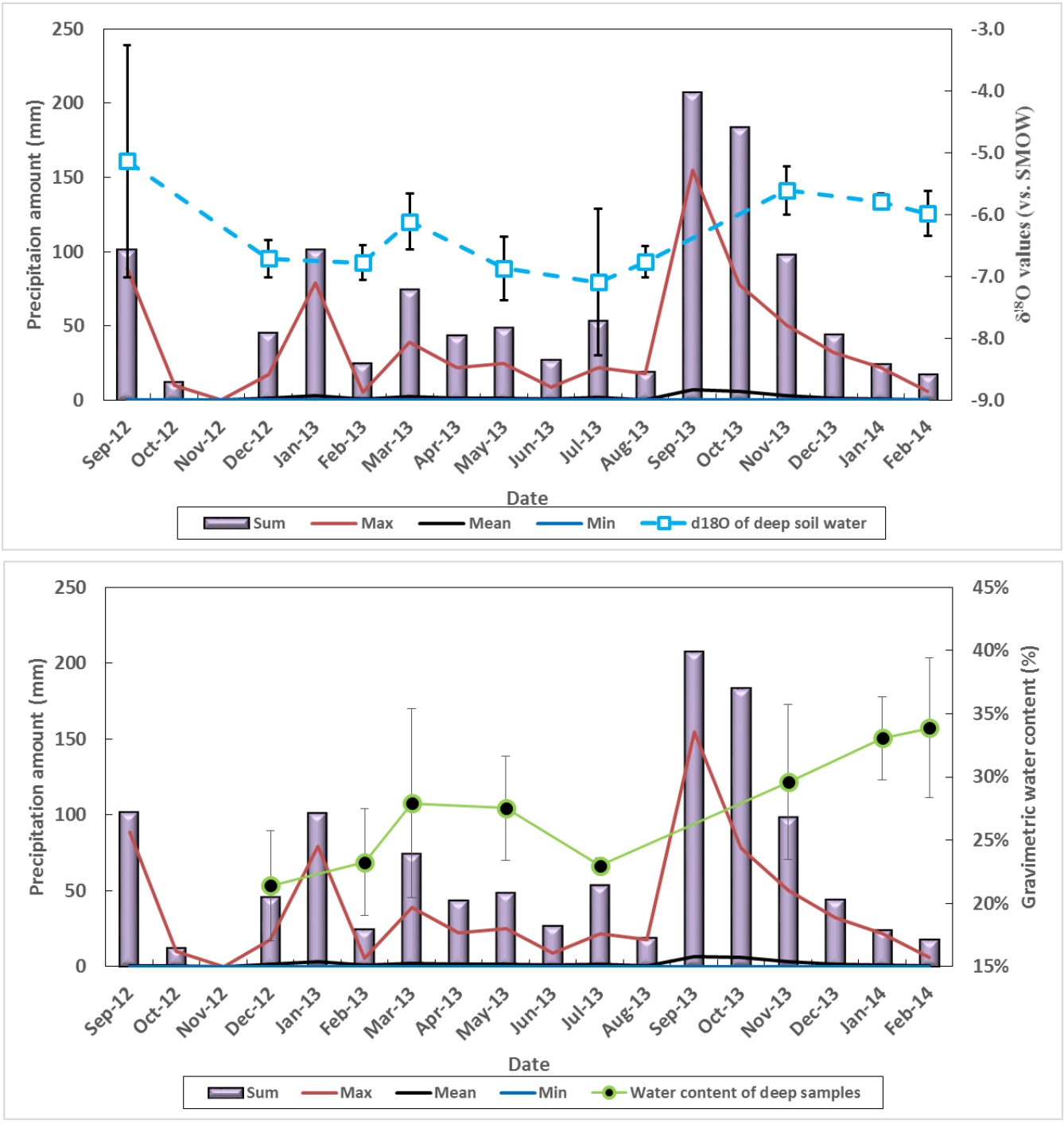

Figure 14: *The amount of precipitation during the interval of study compared to the oxygen isotope composition of deep soil water (80 – 140cm) and the gravimetric water content of the deep soil samples.*

Appendix: Tables

Fractionation Test: Molecular sieve 5A and Extractions			
δD (‰ vs. SMOW)			
Run Date	DI_{Water}	$DI_{zeolite}$	DI_{ex}
20-Mar-14	-3.6	-3.7	-4.2
20-Mar-14	-3.2	-3.6	-6.2
20-Mar-14		-3.5	

Table III*: Data obtained during tests for the presence of fractionation during cryogenic vacuum distillation and from the use of molecular sieve 5A. 50ml of DI water from Austin, TX was collected and 8ml of that water was vacuum distilled (extracted) on March 17, 2014. Extracted DI water was refrigerated and treated as a real sample. On the same day, molecular sieve were placed in 4ml of DI water collected and refrigerated for 6 hours. Two refrigerated DI water samples, three extracted DI water samples, and two DI water with molecular sieve 5A samples were ran on the IRMS for hydrogen isotope composition at The University of Texas at Austin at the same time.*

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